Stereomerisierung der α-Bromallozimtsäure und eine vorläufige Bemerkung über das Additionsprodukt von Bromwasserstoff zu Phenylpropiolsäure

Von Hazime KASIWAGI

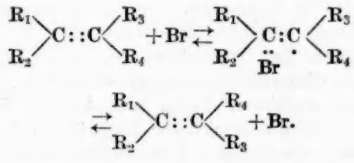
(Eingegangen am 6, August, 1951)

Bei zahlreichen Äthylenverbindungen ist es als Sauerstoffeffekt wohl bekannt, dass sie mit Bromwasserstoff in Gegenwart von Luft, Sauerstoff oder einem gewissen Peroxyde reagieren, und daraus das "abnormale," *d. h.* das zur Markownikowschen Regel in Widerspruch stehende Additionsprodukt bilden *bzw.* durch die sterische Umlagerung in ihre geometrischen Isomeren verwandeln *u. s. w.* Dieser Effekt beruht wesentlich auf einer Kettenreaktion, die durch das freie organische Radikal hervorgerufen wird. Dies letztere ist aus der Äthylenmolekel durch Addition des bei der Reaktion entstandenen Bromatoms als Reaktionsintermediat gebildet. Diese Auffassung ist heute festgestellt worden durch die Tatsache, dass derselbe Effekt durch Anwesenheit von einem "Antioxidant," *z. B.* Brenzkatechin, stark oder ganz verzögert wird.

Der Verfasser beabsichtigt den Vorgang zu untersuchen, wie der sauerstoffeffekt bei den Substanzen auftritt, die eine dreifache Bindung haben. Zu diesem Zwecke ist die Phenylpropiolsäure ausgewählt worden. Über die Addition von Bromwasserstoff zu dieser Substanz haben früher A. Michael und G. H. Shadinger bereits Bericht erstattet,[1] dass sie nämlich, der Verschiedenheit der gebrauchten Lösungsmitteln gemäss, bald α-Bromzimtsäure, bald β-Bromzimtsäure als Produkt erhalten haben. Bemerkenswert ist dabei, dass Phenyl und Carboxyl-gruppe immer eine *trans*-Stellung miteinander einnehmen. Hierauf fassen sie die Bildung solcher Säuren nur als den Effekt verschiedener Lösungsmittel auf, in den man den Bromwasserstoff auf Phenylpropiolsäure reagieren lässt, und infolgedessen lehnen den Kettenmechanismus durch Sauerstoffeffekt ab. Bei dem jetzigen Stand der Kenntnisse muss aber die Möglichkeit geprüft werden, dass die Reaktion durch Mechanismus des Sauerstoffeffekts herbeigeführt würde, was die Entstehung der verschiedenen Säuren zur Folge haben mag. Ferner wird man auch wohl mit Recht diejenigen Bromzimtsäuren, mindestens einen Teil derselben, sei es auch gering, als die sich wegen der sekundären Umlagerung der *cis*- oder Bromallozimtsäuren gebildeten *trans*-Säuren ansehen können.

Zur Erklärung dieser Fragen werden hier die Beobachtungen über die Stereomerisierung der α-Bromallozimtsäure und über die Addition des Bromwasserstoffs zu Phenylpropiolsäure mitgeteilt, die von mir in Gegenwart von Brenzkatechin durchgeführt worden ist.

Betreffs der sterischen Umlagerung der α-Bromallozimtsäure ist die Tatsache schon längst bemerkt worden, dass sie durch Einwirkung einer kleinen Menge von Brom (noch besser, unter dem Sonnenlicht)[2] oder der Wärme[3] zustande kommt. Da wird übrigens die Umlagerung des einen geometrischen Isomeren in das andere durch Einwirkung von Bromwasserstoff nach der nachstehenden Formel des Dissoziationsgleichgewichts, durchgeführt, wenn die infolge des Sauerstoffeffekts entstandenen Radikale sich miteinander nicht vereinigen oder die Atome (H, Br *u. a.*) nicht einnehmen.[4]



Die Isomerisierung Isostilbens in Stilben durch Bromwasserstoff, deren Verlauf in Gegenwart von Licht, Sauerstoff oder Peroxyde stark beschleunigt wird,[5] ist ein typisches Beispiel, das durch den oben erklärten Mechanismus vor sich geht.

Anderseits wird die Umwandlung des Maleinsäuremethylesters ins Fumaroid durch Ein-

(1) *J. Org. Chem.*, **4**, 128 (1939).

(2) R. Stoermer und P. Heymann, *Ber.*, **46**, 1258 (1913).

(3) J. J. Sudborough und K. J. Thompson, *J. Chem. Soc.*, **83**, 686 (1903).

(4) F. R. Mayo und C. Walling, *Chem. Rev.*, **27**, 404 (1940).

(5) Y. Urushibara und O. Simamura, Dieses Bulletin, **13**, 566 (1938); Y. Urushibara, *J. Chem. Soc. Japan*, **60**, 717 (1938).

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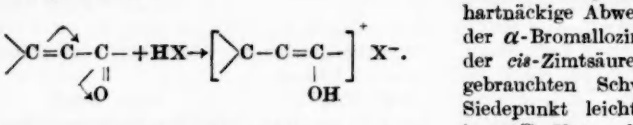
wirkung von Bromwasserstoff,[6] abweichend von denen der dem Stilben ähnlich gebauten Verbindungen, weder durch Sauerstoff beschleunigt noch durch Brenzkatechin unterdrückt wird, aber durch Chlorwasserstoff durchgeführt, womit der Sauerstoffeffekt nicht in Frage kommen kann. Dies weist darauf hin, dass der Vorgang nicht etwa durch das durch Sauerstoffeffekt hervorgerufene Radikal gefördert wird, sondern wohl durch eine elektromerische Verschiebung der Doppelbindung wegen der Protonaufnahme des anliegenden Carbonylsauerstoffs.



Wenn man α-Bromallozimtsäure in einem gewissen, den Bromwasserstoff enthaltenden Lösungsmittel auflöst und sie mehrere Stunden stehen lässt, so verwandelt sie grösstenteils in die *trans*- *d. h.* α-Bromzimtsäure, was man wohl durch den Mechanismus der Kettenreaktion erklären kann, die das durch Sauerstoffeffekt hervorgebrachte Bromatom enthält. Ferner kann man sich vorstellen, dass diese Auslegung sich dadurch bestätigt, dass die oben genannte Isomerisierung stark gehemmt wird von einer Substanz, *z. B.* Brenzkatechin, die den Sauerstoffeffekt zurückhalten kann.

Ferner hat man die Tetrachlorkohlenstofflösung der α-Bromallozimtsäure unter stetigem Chlorwasserstoffstrom auf längere Zeit erhitzt, was die Isomerisierung der zuständigen Säure in *trans*-Säure zur Folge gehabt hat, obzwar die Umwandlung dadurch nur partiell gewesen und viel langsamer als durch Bromwasserstoff oder Brom verlaufen sein mag.

Folglich hat man bewiesen, dass die α-Bromallozimtsäure durch den beiden Mechanismen isomerisieren kann, wie Allozimtsäureester,[7] der die struktuelle Eigentümlichkeiten der oben erwähnten beiden Reihen von Verbindungen hat, *d. h.* der Stilbenreihe, so wie der Maleinsäure.

Die Fähigkeit der Broms, die Isomerisierung der α-Bromallozimtsäure zu verursachen, führt zur Vermutung, daß diese auch durch Jod statt findet. Dies ist unter einer Bedingung der Fall. Nämlich wird die allo-Säure mit Jod in geschmolzenem Rohr vermengt und ein viertel Stunde auf 175°—180° erhitzt, dann wird die Wärmeisomerisierung der *cis*-Säure etwas beschleunigt und sie verläuft um 37.4 Prozente, während ihr Wert in der Abwesenheit des Jods höchstens halb des oben genannten Prozentsatzes (18%) beträgt. Diese Umlagerung würde wahrscheinlich dank des Jodatoms, wie die der *cis*-Zimtsäure verlaufen[8]. Unter den anderen Bedingungen, worin man eine Wirkung des Broms deutlich erkennen kann, entfernt sich jedoch das experimentelle Resultat weit von der Erwartung und man kann dabei keine Isomerisierung beobachten. Sie ist sogar gar nicht aufgetreten, wenn man auch α-Bromallozimtsäure in Gegenwart von Jod mit dem Lösungsmittel wie Tetrachlorkohlenstoff in seinem Siedepunkt lang erhitzt hat. Diese hartnäckige Abwehrung gegen Isomerisierung der α-Bromallozimtsäure ist etwas anders bei der *cis*-Zimtsäure, die im als Lösungsmittel gebrauchten Schwefelkohlenstoff bei seinem Siedepunkt leicht in *trans*-Säure übergehen kann.[9] Unter dieser Bedingung würde die Isomerisierung vielleicht durch Jod ein wenig gehemmt werden, da der Wert der Isomerisierung in seiner Gegenwart unmerkbar klein ist, der sonst einige Prozente beträgt. Dass diese Erscheinung darauf nicht beruht, dass die Umwandlung der α-Bromzimtsäure umgekehrt in ihren *cis*-Isomer, nämlich in α-Bromallozimtsäure, durch Jod erregt wird, wie durch die längere Bestrahlung mit ultraviolettem Licht,[10] ist davon festgestellt worden, dass die α-Bromzimtsäure, nach dem gleichen Verfahren mit Jod behandelt, gar nicht isomerisiert ist.

Überdies zeigt das Jod eine sehr auffallende Erscheinung, dass es nämlich wie Brenzkatechin, aber auf eine etwas schwächere Weise, die durch Bromwasserstoff katalysierte Stereomerisierung hemmt. Da die Isomerisierung der α-Bromallozimtsäure durch Bromwasserstoff, wie oben erwähnt, grösstenteils durch Sauerstoffeffekt geleistet wird, ist es zweifellos anzunehmen, dass das Jod auf diesen Effekt schädlich wirkt.

Der grösste Teil der Produkte, die man aus Phenylpropiolsäure durch direkte Einwirkung von Bromwasserstoff auf ihre Benzollösung erhält, ist α-Bromzimtsäure, was Michael und Shadinger bestätigt haben. Warum wird die α-Bromallozimtsäure überhaupt nicht erhalten? Weist der Misserfolg, die α-Bromallozimtsäure vom Reaktionsgemisch aus zu isolieren, nicht darauf, dass der Sauerstoffeffekt sich an dieser Reaktion beteilige?

Gesetzt, es sei richtig diese Vermutung, dann muss die Reaktion des Bromwasserstoffs auf

(6) O. Simamura, Dieses Bulletin, **14**, 22 (1939).
(7) O. Simamura, Dieses Bulletin, **14**, 29 (1939).
(8) R. G. Dickinson und H. Lotzkar, *J. Am. Chem. Soc.*, **59**, 472 (1937); A. Berthoud und Ch. Urech, *J. chim. phys.*, **27**, 291 (1930).
(9) C. Liebermann, *Ber.*, **23**, 512 (1890).
(10) R. Stoermer und P. Heymann, *Ber.*, **46**, 1251 (1913).

Phenylpropiolsäure unter Benutzung von Antioxidant anders als die der gewöhnlichen Addition, *d. h.* nicht nach Vorschrift von Michael und Shadinger verlaufen. Dies ist tatsächlich der Fall, und die Wirkung des Brenzkatechins ist erheblich. Man konnte keine α-Bromzimtsäure in den Additionsprodukt finden.

Beschreibung der Versuche

α-Bromallozimtsäure wird dargestellt durch die Behandlung des Zimtsäuredibromids mit alkoholischer Kalilauge. Da die bezweckte Säure mit dem *trans*-Isomeren vermengt ist, werden die beiden Isomeren Vermöge des Unterschiedes der Löslichkeit ihrer Bariumsalze getrennt. Das Exemplar, das man sich aus dem leichten Petroleumäther-Chloroform dreimal umkristallisiert hat, ist bei 119—120° geschmolzen.

I. Isomerisierung durch Bromwasserstoff

(a) **Wirkung desselben allein.**—α-Bromallozimtsäure wird in schwefelfreiem Schwefelkohlenstoff aufgelöst, worin das Bromwasserstoffgas vorher durchgeleitet worden ist, und man lässt die Lösung auf die erforderliche Zeit stehen. Die Lösung wird zum Befreien von Bromwasserstoff mit Wasser durchschüttelt und abdestilliert. Löst man den erhaltenen gelblichen Rückstand in Ammoniakwasser auf und versetzt ihn mit einer ziemlich konzentrierten Bariumchloridlösung, so scheidet sich der Niederschlag so fort ab, was das Übergehen der gebrauchten Allosäure in die *trans*-Säure zeigt. Die unveränderte Allosäure aber bleibt in der Lösung als lösliches Bariumsalz zurück. Dann werden der Niederschlag und das Filtrat voneinander getrennt, jedes für sich, mit Salzsäure angesäuert und mit Äther mehrmals ausgeschüttelt. Nach dem Trocknen der beiden Ätherlösungen mit wasserfreiem Natriumsulfat, destilliert man den Äther ab und wiegt die erhaltenen Rückstände.

Zur Feststellung, dass diese beiden Substanzen reine Isomere sind, schmilzt man sie jede für sich mit den vorbreiteten Exemplaren zusammen, entweder ohne weitere Behandlung, oder nach Umkrystallisation aus dem leichten Petroleumäther-Chloroform, oder aus dem Tetrachlorkohlenstoff. Die zur Feststellung der isomerisierten Säure angewandte α-Bromzimtsäure ist nach dem Verfahren von Sudborough und Thompson[3] aus α-Bromallozimtsäure dargestellt worden. Die umkrystallisierte *trans*-Säure hat den Schmelzpunkt 130.5—131°. Über die Wirkung des Bromwasserstoffs gibt die Tabelle 1 eine folgerichtige Erklärung ab.

(b) **Einfluss des Lichts.**—Diese Reihe von Versuchen ist in der Dunkelkammer durchgeführt worden, die Luft aus dem Reaktionsraum aber nicht weggenommen, obgleich die Versuche unter strengem Luftausschluss ausgeführt werden sollen, um daraus eine sichere Schlussfolgerung über den Sauerstoffeffekt in dieser Stereomerisierung zu ziehen. Aber die Zahlen (Tab. 2) werden doch deutlich zeigen, dass die Abwesenheit des Lichts wahrscheinlich auf die Isomerisierung einen schädlichen Einfluss ausübt.

Die Werte auf der Tabelle 3 sind unter anderen Bedingungen erhalten worden. Das Lösungsmittel wird unter Lichtausschluss und im Stickstoffstrom in das Reaktionsgefäss eindestilliert, worin die Allosäure eingesetzt ist, um die Luft aus dem Reaktionsraum und aus der Lösung vollkommen auszuschliessen, und dann wird Bromwasserstoff, dessen Entwicklungsapparat auch mit Stickstoff voraus gesättigt ist, durchgeleitet. Man kann aber die Verminderung des Isomerisierungswerts aus

Tabelle 1

Anfangsmaterial, g.	CS_2, cc.	Reaktionsdauer, Stdn.	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.45	20	48	—	0.40	>88.9
0.125	13	24	0.116	0.108	93.1
0.191	20	24	0.184	0.170	92.4
0.689	40	24	0.663	0.652	98.3

Tabelle 2

Anfangsmaterial, g.	CS_2, cc.	Reaktionsdauer, Stdn.	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.138	13	24	0.127	0.099	78.0
0.182	18	48	0.169	0.124	73.4
0.199	20	48	0.181	0.135	74.6

Tabelle 3

Anfangsmaterial, g.	CS_2, cc.	Reaktionsdauer, Stdn.	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.944	45	48	0.913	0.648	71.0
0.567	30	48	0.547	0.382	69.8

diesen Zahlen nicht deutlich ersehen.

(c) **Wirkung des Brenzkatechins.**—Die zuständige Säure wird im mit Bromwasserstoff vorausgesättigten Schwefelkohlenstoff mit Brenzkatechin aufgelöst und stehen lassen. Die Menge des umgewandlten Säure nimmt beträchtlich ab, wie man aus der Tabelle 4 ersehen kann.

Man kann den Einfluss des Brenzkatechins auch deutlich erkennen, selbst wenn die durch Bromwasserstoff katalysierte Isomerisierung verhältnissmässig klein ist. Zu solchen Umstände kann man gelangen durch Abkürzen der Reaktionsdauer oder durch Anwedung von Lösungsmitteln, wie Tetrachlorkohlenstoff, worin das Anfangsmaterial schwer löslich ist und der grösste Teil desselben als Niederschlag unverändert bleibt. Die Tabelle 5 zeigt diese Verhältnisse.

Die zahlen auf der Tabelle 6 sind genügend, um damit zuzeigen, die hemmende Kraft des Brenzkatechins unter dem Gebrauch von einer äusserst geringen Menge desselben absinkt.

II. Wirken der Halogene

Das Wirken des Broms enthält kein Problem in sich, aber mit Jod steht es ganz anders. Wenn man auch die Tetrachlorkohlenstofflösung sieden lässt, tritt die erwartete Wirkung nicht auf, und es scheint, dass die Stereomerisierung dagegen gehemmt wird. Auf der Tabelle 7 sieht man einige Beispiele über die Wirkung der Halogene.

Ferner, wenn man die mit Jod beigemengte α-Bromallozimtsäure in den vorher mit Bromwasserstoff durchströmten Schwefelkohlenstoff auflöst, wird die sonst durch Bromwasserstoff zu katalysierende Isomerisierung stark verzögert (Tabelle 8). Auf der Tabelle sind die beiden Werte der Isomerisation, die durch Bromwasser-

Tabelle 4

Anfangsmaterial, g.	Brenzkatechin, g.	CS_2, cc.	Reaktionsdauer, Stdn.	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.530	0.0285	40	24	0.513	0.035	6.6
0.515	0.028	40	24	0.500	0.031	6.2

Tabelle 5

Anfangsmaterial, g.	Brenzkatechin, g.	Lösungsmittel, cc.	Reaktionsdauer	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.838	unbenutzt	40 CS_2	10 Min.	0.828	0.019	2.3
0.860	0.011	40 CS_2	10 Min.	0.849	0.004	0.5
0.854	0.057	40 CS_2	10 Min.	0.839	0.006	0.7
0.995	unbenutzt	40 CCl_4	36 Stdn.	0.972	0.060	6.2
0.556	0.0285	20 CCl_4	36 Stdn.	0.540	0.003	0.6

Tabelle 6

Anfangsmaterial, g.	Brenzkatechin, g.	CS_2, cc.	Reaktionsdauer, Stdn.	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.121	0.0015	12	22	0.108	0.075	69.4
0.196	0.0017	20	48	0.189	0.124	65.6

Tabelle 7

Anfangsmaterial, g.	Halogen, g.	Lösungsmittel, cc.	Reaktionsdauer, Stdn. auf Zimmer Temperatur	Reaktionsdauer, Stdn. auf Siedepunkt von CCl_4	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.090	0.0055 Br_2	7 CS_2	48	—	0.082	0.078	95.1
0.217	0.0042 Br_2	15 CS_2	96	—	0.203	0.190	93.6
0.098	0.0073 J_2	7 CS_2	48	—	0.095	0.001	1.2
0.215	0.0070 J_2	15 CS_2	96	—	0.200	0.002	1.0
0.547	0.0230 J_2	60 CCl_4	55	18	0.530	0.004	0.8
0.563	0.1003 J_2	35 CCl_4	55	18	0.546	0.002	0.4
0.498	unbenutzt	55 CCl_4	55	18	0.475	0.016	3.7
0.177	unbenutzt	20 CCl_4	85	12	0.162	0.008	5.1

Tabelle 8

Anfangsmaterial, g.	Antioxidant, g.	Lösungsmittel, cc.	Reaktionsdauer, Stdn.	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.689	unbenutzt	40 CS_2	24	0.663	0.652	98.3
0.530	0.0285 Brenzkatechin	40 CS_2	24	0.513	0.035	6.6
0.772	0.0565 J_2	40 CS_2	24	0.751	0.083	11.1
0.995	unbenutzt	40 CCl_4	36	0.972	0.060	6.2
0.556	0.0285 Brenzkatechin	20 CCl_4	36	0.540	0.003	0.6
0.996	0.061 J_2	40 CCl_4	36	0.977	0.014	1.4

Tabelle 9

Anfangs-material, g.	Lösungs-mittel, cc.	Reaktionsdauer, Stdn. auf Zimmer Temperatur	Reaktionsdauer, Stdn. auf Siedepunkt von CCl_4	Totalsumme beider Isomeren, g.	Isomerisierter Teil, g.	Isomerisierter Teil, %
0.391	20 CS_2	48	—	0.371	0.000	0.0
0.245	30 CCl_4	76	20	0.226	0.034	15.0
0.405	50 CCl_4	76	20	0.380	0.062	16.3

stoff sowohl in Gegewart von Brenzkatechin wie auch in dessen Abwesenheit ergeben werden, zum Vergleich wieder angegeben.

III. Einfluss des Chlorwasserstoffs

Wird die α-Bromallozimtsäure in Tetrachlorkohlenstoff aufgelöst, und unter Hindurchleiten des Chlorwasserstoffstroms gekocht, so erfährt sie eine Stereomerisierung, deren Menge deutlich grösser ist, als die der nur von Wärme hervorgebrachten Umwandlung (Tabelle 9). Bei gewöhnlicher Temperatur findet keine merkliche Veränderung statt.

IV. Direkte Einwirkung des Bromwasserstoffs auf Phenylpropiolsäure

(a) **In Benzol.**—Man löst 1 g. Phenylpropiolsäure in 15 cc. Benzol auf, leitet den getrockneten Bromwasserstoff eine Stunde lang durch, und lässt sie eine Nacht stehen; dann wäscht man die Lösung einmal mit Wasser, dampft das Lösungsmittel ab, und man erhält 1.47 g. (95% d. Theor.) sauren Rückstand als Additionsprodukt. Dieser Rückstand besteht aber aus mindestens zweierlei Säuren, da er beim Zusazt von konzentrierter Bariumchloridlösung zu seiner ammoniakalischen Lösung neben dem löslichen Bariumsalz eine kleine Menge von löslichem gibt. Die Menge der Säure, die aus dem ersteren durch Ansäuerung mit verdünnter Salzsäure erhalten wird, beträgt 1.29 g. Nach Umkrystallisation aus dem leichten Petroleumäther-Chloroform schmiltzt sie bei 128.0—129.5°, und stimmt mit α-Bromzimtsäure überein. Dagegen kann man aus dem löslichen Bariumsalz keine einheitliche Säure erhalten. Sie wird mit α-Bromallozimtsäure zusammengebracht, um dann bei einer weit tieferen Temperatur zu schmelzen.

(b) **In Gegenwart von Brenzkatechin im gleichen Lösungsmittel.**—In Gegenwart von genanntem Antioxidant lässt man den Bromwasserstoff auf die Benzollösung von 2 g. reiner Phenylpropiolsäure reagieren. Nach der Addition und dem Abdampfen des Benzols erhält man den Rückstand, der den sauren Teil enthält, der das lösliche Bariumsalz gibt. Diese Säure, aus Tetrachlorkohlenstoff umkrystallisiert, beträgt 1.25 g. Ihr Schmelzpunkt liegt bei 151—6°, während der des Gemisches mit α-Bromzimtsäure wohl unter 90° liegt, welche Tatsache zwanglos zur Feststellung führt, dass es keineswegs α-Bromzimtsäure ist, die in Abwesenheit von Antioxidant das Hauptprodukt gewesen ist. Unter den Reaktionsprodukten findet man ferner 1.22 g. sauren Stoff, der unlösliches Salz gibt und sich mit keiner einheitlichen Säure identifizieren lässt, von α-Bromallozimtsäure ganz zu schweigen. Abgesehen davon, dass die Trennungsmethode nicht scharf genug ist, um einzelne Stoffe völlig zu isolieren, kann man schliessen: es ergebe sich keine α-Bromzimtsäure bei dieser Reaktion.

Zusammenfassung

Die Einwirkung von Bromwasserstoff auf α-Bromallozimtsäure ruft keine Bildung des Zimtsäuredibromids hervor, sondern die Stereomerisierung, *d. h.* ihre Umwandlung in den *trans*-Isomere, α-Bromzimtsäure. Diese Umwandlung kann auch sowohl durch Brom als durch Chlorwasserstoff hervorgebracht werden, durch Jod aber geht dies keineswegs, wobei im Gegenteil der sonderbare Effekt desselben beobechtet wird, dass es auf die von Bromwasserstoff katalysierte Isomerisierung schädlich wirkt. Solche störende Wirkung auf die Isomerisierung tritt in Gegenwart von Brenzkatechin, einem bekannten Antioxidant, noch deutlicher auf im vorhergehenden fall. Diese Erschcinungen führen zwanglos zur Annahme, dass diese Reaktion hauptsächlich von den Mechanismus des Sauerstoffeffekts entstandenen Atomen oder freien Radikalen erregt werde. Doch darf man hier die Teilnahme des Ionenmechanismus, wenn diese auch gering sein mag, gar nicht wegleugnen.

Es sei noch hinzugefügt, dass die α-Bromzimtsäure, die aus Phenylpropiolsäure, gelöst in Benzol, durch unmittelbare Addition des Bromwasserstoffs erhalten wird, ihre Bildung dem Sauerstoffeffekt verdankt.

Zum Schluss muss der Verfasser den Herren Prof. Y. Urushibara und Prof. O. Simamura für ihre freundlichen Leitungen, sowie seinen Arbeitsgenossen für ihren Beistand durch lebhafte Diskussion über diesen Gegenstand den herzlichen Dank aussprechen.

Chemisches Institut,
Fakultät der Naturwissenschaften,
Tokyo Universität

The Salt Effect in the Aniline-Formaldehyde Condensation

By Yoshiro OGATA, Masaya OKANO and Tsutomu YAMAMOTO

(Received Octover 23, 1951)

In our previous paper the kinetic study of the aniline-formaldehyde condensation in aqueous hydrochloric acid media has been reported.[1] The rate has been found to be second-order with respect to the initial concentration of aniline and first-order with respect to the sum of the concentrations of formaldehyde and methylene-anilines present. The purpose of the present investigation is to find the effect of inorganic salts on the rate of this reaction in aqueous hydrochloric or sulfuric acid media. The results show that the catalytic action of the salts is explicable in terms of the primary and secondary salt effects.[2]

Experimental

Materials and General Procedures are substantially the same as those in the previous paper.[1]

Experimental Results are shown in Fig. 1 and Table 1. Fig. 1 shows the effect of *p*H on the

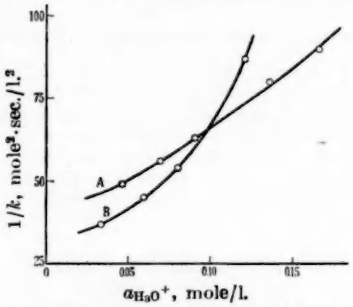


Fig. 1.—Relationship between $1/k$ and $a_{H_3O^+}$: A, 0.10 *M* $C_6H_5NH_2$+0.10 *M* CH_2O+0.15~0.30 *M* HCl; B, 0.10 *M* $C_6H_5NH_2$+0.10 *M* CH_2O+0.10~0.30 *M* H_2SO_4.

Table 1

The Effect of Various Salts on the Rate of the Aniline-Formaldehyde Condensation (25.0±0.1°C)

(A) Concentrations of reactants in original solutions: Aniline 0.1 *M*, HCl 0.2 *M*, Formaldehyde 0.1 *M*.

Added salt	*M*	*p*H	$a_{H_3O^+}M$	$k_f\times10^4$ (l/sec.)	$1/k_e$ (mole²·sec./l.²)	$1/k_c$ (mole²·sec./l.²)	μ_e	μ_c	β
None		1.05	0.090	1.57	64		0.20		
NaCl	0.50	0.99	0.105	1.88	53	67	0.70	0.22	0.6
〃	1.00	0.93	0.120	2.12	47	75	1.20	0.23	0.7
〃	2.00	0.79	0.160	2.66	38	89	2.20	0.30	0.9
KCl	1.00	0.96	0.110	2.32	43	71	1.20	0.22	0.8
$MgCl_2$	0.50	0.92	0.120	2.61	38	75	1.70	0.23	0.8
KBr	1.00	0.97	0.110	2.49	40	71	1.20	0.22	1.0
Na_2SO_4	0.10	1.40	0.040	2.78	36	46	0.50	0.15	0.9
K_2SO_4	0.10	1.42	0.038	2.82	35	45	0.50	0.15	0.9

(B) Concentrations of reactants in original solutions: Aniline 0.1 *M*, H_2SO_4 0.1 *M*, Formaldehyde 0.1 *M*.

None		1.48	0.033	2.67	37		0.30		
Na_2SO_4	0.10	1.64	0.023	3.87	26	34	0.60	0.26	1.1
〃	0.20	1.79	0.016	4.81	21	33	0.90	0.22	1.0
〃	0.30	1.84	0.014	5.63	18	32	1.20	0.22	0.9
K_2SO_4	0.10	1.65	0.023	3.84	26	34	0.60	0.26	1.1
$MgSO_4$	0.10	1.56	0.028	3.81	26	34	0.70	0.28	1.0
KBr	1.00	1.28	0.053	3.52	29	42	1.30	0.41	0.6
KCl	1.00	1.29	0.051	3.38	29	42	1.30	0.41	0.6

(1) Ogata, Okano and Sugawara, *J. Am. Chem. Soc.*, **73**, 1715 (1951).

(2) La Mer, *Chem. Rev.*, **10**, 179 (1932); Moelwyn-Hughes, "Kinetics of Reactions in Solution," Clarendon Press, Oxford, 1933, pp. 184.

rate with constant stoichiometric initial concentrations of aniline (0.1 M) and formaldehyde (0.1 M). In the figure, k is equal to k_f/a^2, where a is the initial concentration of aniline and k_f, the pseudo-first-order constant with respect to formaldehyde present. Table 1 tabulates the effect of the addition of several salts. Here, k_c corresponds to k described above and μ_c is the ionic strength of the solution; the definitions of k_c, μ_c and β will be given in the next paragraph. The salts employed are those alone which afford homogeneous solutions during rate measurements and do not interfere with titrimetric analyses.

Discussion of Results

Fig. 1 suggests that in sulfuric acid solution more attention should be paid to the concentration of free arylamino group together with undissociated arylammonium sulfate upon the rate than in hydrochloric acid solution. In order to derive the generalized rate equation in which undissociated aniline hydrochloride is taken into account as in dimethylaniline-formaldehyde condensation,[3] equilibria

$$\mathrm{ArNH_2} + \mathrm{HCl} \rightleftharpoons \mathrm{ArNH_3Cl} \quad \text{(a)} \quad K_a$$
$$\mathrm{ArNH_3Cl} \rightleftharpoons \mathrm{ArNH_3^+} + \mathrm{Cl^-} \quad \text{(b)} \quad K_b$$

should be considered. Here, K_a is the average equilibrium constant of the formation of hydrochlorides of aniline and its condensate; K_b, that of their ionization. Consequently, the initial concentration of aniline is expressed as

$$a \doteqdot \sum[\mathrm{ArNH_2}] + \sum[\mathrm{ArNH_3Cl}] + \sum[\mathrm{ArNH_3^+}]$$

or

$$\sum[\mathrm{ArNH_2}] = a/\{(K_A/K_W)(1+[a_{\mathrm{Cl^-}}/K_b])+1\}$$

in which K_A is the average ionization constant of aniline and its condensate, $\mathrm{ArNH_2}$, and K_W is the ion product of water. Introduction of this value into the rate equation previously given,[1] *i.e.*,

$$\mathrm{d}x/\mathrm{d}t = K a_{\mathrm{H_3O^+}} (\sum[\mathrm{ArNH_2}])^2 (f-x) \qquad (K\text{: a constant})$$

leads to

$$\mathrm{d}x/\mathrm{d}t = \frac{K a_{\mathrm{H_3O^+}} a^2 (f-x)}{\left\{1+\frac{K_A}{K_W}\left(1+\frac{a_{\mathrm{Cl^-}}}{K_b}\right)a_{\mathrm{H_3O^+}}\right\}^2} = k_f(f-x) \qquad (1)$$

in which $a_{\mathrm{H_3O^+}}$ etc. are the activities of the subscripted substances, $\mathrm{H_3O^+}$ etc. Hence, the relation between a^2/k_f and $a_{\mathrm{H_3O^+}}$ is given by

$$\frac{1}{k} = \frac{a^2}{k_f} = \frac{1}{K a_{\mathrm{H_3O^+}}} + \frac{2K_A}{KK_W}\left(1+\frac{a_{\mathrm{Cl^-}}}{K_b}\right) + \frac{K_A^2}{KK_W^2}\left(1+\frac{a_{\mathrm{Cl^-}}}{K_b}\right)^2 a_{\mathrm{H_3O^+}} \qquad (2)$$

The plot of $1/k$ against $a_{\mathrm{H_3O^+}}$ expressed in two curves in Fig. 1 should be consistent with this equation (2). If the equation is compared with equation (18) in the previous paper, it is apparent that the added terms $1/Ka_{\mathrm{H_3O^+}}$ and $a_{\mathrm{Cl^-}}/K_b$ are related with free aniline and undissociated aniline hydrochloride, respectively. In hydrochloric acid media, $a_{\mathrm{Cl^-}}/K_b$ shows the ratio $[\mathrm{ArNH_3Cl}]/[\mathrm{ArNH_3^+}]$, and $1/K a_{\mathrm{H_3O^+}}$ may be negligible in comparison with the other terms. In sulfuric acid media, however, the latter term should probably not be eliminated.

The dissociation of excess hydrochloric acid and that of hydrochlorides of aniline together with its condensate will be affected by adding salt. Although pH increases generally by adding inorganic salt into aqueous acid, the present results show that the pH decreases and therefore the concentration of hydrochloric acid ($\mathrm{HCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{Cl^-}$) as well as free aniline seems to increase as the amount of salt increases. Surely this change in pH will give rise to the change in the rate, *i.e.*, "secondary salt effect". The variation of k with pH was estimated from the curves in Fig. 1, while the effect of an increase in ionic strength on the rate will be considered later. These presumptive values of rate constant k_c and ionic strength μ_c in Table 1, where no inorganic salt is contained in the solution at the same pH's as shown in the third column of the same line, were measured by employing these curves. On the other hand, the change of the dissociation of arylammonium hydrochlorides seems to be difficult to evaluate, but probably it is reasonable to suppose that the value of $1/k$ decreases as the mean value of K_b increases by the addition of chloride in aniline sulfate solution. (See equation (2).)

The effect of salts on activity coefficients of reactants, so-called "primary salt effect," is expressed as equation (3) for the reaction between a neutral molecule and an ion at relatively high concentration.[4]

$$k = k_0(1+\mu\beta) \qquad (3)$$

where k is a rate constant with ionic strength μ, k_0, that with the ionic strength zero, and β, a constant. In hydrochloric acid medeia, the above values of k_c together with those of

(3) Ogata and Okano, *J. Am. Chem. Soc.*, **72**, 1459 (1950).

(4) Glasstone, "Text-book of Physical Chemistry", D. Van Nostrand Company, New York, 1940, pp. 1115.

k_e, *i. e.*, the values of experimentally found, are expressed as

$$1/k_0=(1+\mu_e\beta)/k_e \quad (4)$$

$$1/k_0=(1+\mu_s\beta)/k_s \quad (5)$$

Therefore, β can be calculated by means of an equation

$$\beta=\{(1/k_e)-(1/k_s)\}/\{(\mu_e/k_e)-(\mu_s/k_s)\} \quad (6)$$

As shown in Table 1, β holds good constancy. In hydrochloric acid media, average value of β is equal to 0.8 and in sulfuric acid media, β, 1.0. Using these values of β and those of k at appropriate oxonium ion activity (*e. g.*, pH=1.5) in Fig. 1, k_0 may be calculated by means of equation (3). The values of k_0 calculated independently by using the data in hydrochloric and sulfuric acid solutions are in agreement; *i. e.*, $k_0=2.09\times10^{-2}$ and 2.11×10^{-2} (l^2./mole.^{2}·sec.), respectively. Abnormal values of β were obtained when either bromide or chloride was added into sulfuric acid media. These facts may be explained by assuming that the mean values of K_b are increased under these conditions. This catalytic effect of anions of salts may be ascribed to the acceleration of the rate-determining attack of carbonium ion $ArNHCH_2^+$ on the carbon atom of the benzene nucleus by attracting proton of the nucleus to the anion. A similar concerted mechanism has been suggested by Swain in other nucleophilic reactions.(5)

Summary

In the hydrochloric or sulfuric acid-catalyzed condensation of aniline with formaldehyde, it was found that the addition of inorganic salt, *e. g.*, sodium chloride or potassium sulfate, increases the rate and this fact is ascribed to the so-called primary and secondary salt effects.

The authors wish to express their thanks to Prof. T. Nishi for the assistance in pH measurement.

Department of Industrial Chemistry
Faculty of Engineering
Kyoto University, Kyoto

(5) Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948); **72**, 2794 (1950).

Spinnability of Liquid. A Visco-elastic State. I. Spinnability and Anomalous Viscosity

By Tsurutaro NAKAGAWA

(Received November 2, 1951)

Introduction

It is well-known that some substances which are usually considered as "liquids" have a marked thread-forming property as is shown by Fig. 1. The so-called mucilaginous fluids, such as egg-white, vitreous humour of the eye, saliva, secretion of the various mucous membranes, mucus from seaweeds, extraction of the root of *Abelmoschus Manihot* Medicus (*Hibiscus Manihot* L.), mucus of a taro, mucus of "nattô" (fermented beans), and other rotten or fermented things, all possess this peculiar property; furthermore in the laboratory, we see the phenomenon in a raw rubber-benzene solution, aq. solution of mercury sulphosalicylic acid, and in some coacervates. When we raise a stirring rod from these liquids, or when the liquids are poured out of a beaker, a very long and fine thread is spun which sometimes reaches a length of 30~40 cm. or more.

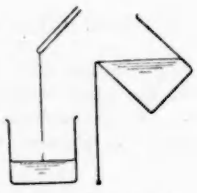


Fig. 1.

To what is this phenomenon attributed? One may ascribe it to the high viscosity which is characteristic of the solution of polymeric substances; but the impropriety of this assumption will be understood by the fact that the other high-viscous polymer solutions, for

example, starch solution, gelatin sol, or agar-agar sol, pectin sol, etc. show no spinnability. Recognizing that the spinnability of liquid is not solely related to the viscous flow, what is the other factor to be added?

Inspection of the examples cited above gives us two general ideas; first, from the chemical point of view, they are high-polymeric solutions, and second, from the physical point of view, they are in the colloidal state. Mechanical properties of these high-polymeric or colloidal states consist of many non-ideal peculiarities: their deformation is non-Hookean, and their flow is non-Newtonian. From the standpoint of relaxation phenomena, the time of mechanical relaxation λ of these high-polymeric, colloidal and the so-called "amorphous" substances is finite. Deviations from the ideal behavior of the mechanical properties of these high-polymeric materials depend chiefly upon this finite relaxation time. Because of the fact that λ is comparable with the time of our observation (t), the mechanical behavior of those amorphous substances usually appears as a relaxation phenomena. According to the relative magnitude of λ to (t), the apparent mechanical behavior of the subject shows much variety; in other words, the time-effect is remarkable in the mechanical properties of high-polymers.

One of the phenomenological treatments to describe systematically these non-ideal, time-sensitive mechanical properties is the theory of the "visco-elastic or elastic-viscous state". By this method, various actual anomalies of the mechanical behavior are described quantitatively as a function of the "magnitudes" of η (viscosity coefficient) and G (elasticity coefficient) and of the "type" of coupling of η and G. Now that our spinnable (thread-forming) liquids are generally high-polymeric or colloidal solutions, the above-stated concept of a visco-elastic state will be applicable to this peculiar mechanical property. Supporting this view, we actually observe some elastic property in these spinnable liquids; a liquid-thread springs back elastically when it breaks, or these liquids in a vessel turn back in the opposite direction when we rotate it in one direction and then hold it.

In this essay, the spinnability of liquids is treated from these points of view.

Tammann and Tampke[1] measured spinnability by the maximum length of a liquid thread formed when a rod is raised from a spinnable liquid as is shown by Fig. 2. This method seems to be the most convenient and popular.

Fig. 2.

Jochims[2] found out that viscosity is not the single factor which causes spinnability and determines the degree of spinnability, and that an elastic scaffolding existing in such a liquid is another important factor.

H. Erbring[3] first treated it systematically and extensively as a colloid-chemical problem; his general conclusion drawn out of his experiments is outlined as follows. He used Tammann and Tampke's principle (Fig. 2) to express the degree of spinnability quantitatively. From his measurements on an extract of flax-seeds, mucilage of quince, solutions of gum Arabic, mercury sulphosalicylic acid, acetyl cellulose, cotton-yellow, aluminium soap, polystyrene, sodium stearate, sodium silicate, polyvinyl alcohol, and viscose etc., some coacervates, for example, a gelatin-phenol coacervate and a gelatin-starch coacervate etc., Erbring gained the following general aspects on the spinnability phenomenon; (a) spinnability does not simply depend upon viscosity of liquid, (b) surface tension also is not an important factor, its influence being negligible for markedly spinnable liquids, (c) a sort of "elasticity" plays a principal rôle in this phenomenon, (d) spinnability is a phenomenon relating to a particular colloid-chemical "state" of a substance, and not to a special chemical species, (e) spinnability seems to be owing to some "structure" in liquid, both a proper fluidity (viscosity) and a proper consistency (structure) being important for the appearance of spinnability, (f) the existence of rod-shape or long-chain molecules in liquid seems to be necessary, (g) structural viscosity (non-Newtonian flow) is closely related to spinnability.

Measurement of Spinnability

As the first step, the author constructed an apparatus for observing quantitatively the degree of spinnability after the Tammann-Erbring method,[3] in which the degree of spinnability is expressed by the maximum length of a liquid thread spun by a rod raised out of the liquid.

(A) **Apparatus**—Since the maximum length of a liquid thread depends appreciably upon the velocity of the ascending of a testing rod,

(1) G. Tammann and R. Tampke, *Z. anorg. allgem. Chem.*, **162**, 1 (1927).

(2) J. Jochims, *Koll. Z.*, **61**, 250 (1932).

(3) H. Erbring, *Koll. Beih.*, **44**, 171 (1936); *Koll. Z.*, **77**, 32, 213 (1936); *ibid.*, **80**, 20 (1937); *ibid.*, **98**, 164 (1942) or *Chem. Abs.*, **36**, 6393 (1942).

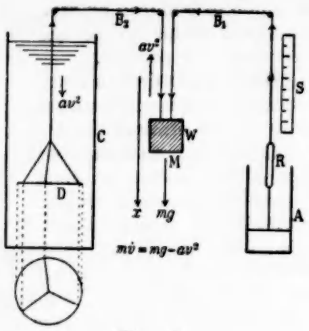


Fig. 3.

R, a velocity controlling device as is shown by Fig. 3 was constructed. The rod R is driven by a weight W and some pulleys, and acceleration of W is suppressed by a damper D moving in water, so that a constant terminal velocity is gained, which is voluntarily controlled if W is changed. The terminal velocity is attained soon after starting.

D is a disc of 16 cm. dia. Weight of W and D is 120 g. and 70 g. respectively, so that the effective driving weight of W is approximately 30 g., assuming empirically that the total frictional resistance at the mechanical contacts is equivalent to about 20 g. Then the velocity of R can be controlled in the neighbourhood of 5 cm./sec. Reproducibility is satisfactory. (Fluctuation of the measured maximum thread length is less than 5 mm.)

(B) Spinnability of simple high-viscous liquids: trivial case of spinnabiliy.— The most simple and trivial type of spinnability is one by very high viscosity of liquid, for then a liquid column is formed between the surface of the liquid and the tip of a rising rod because of the slowness of the liquid supply downward from a rod (Erbring's "Nachliefe-rungsvorgang"). From what value of viscosity does this simple spinnability due to the slow supply appear? The author experimented as follows.

As the comparatively high-viscous liquids whose flow are ideally Newtonian, exhibiting neither elastic property nor structural viscosity (anomalous viscosity), two solutions were taken, namely (a) conc. aq. solution of sucrose and (b) aq. solution of water glass (sodium silicate). Sucrose is suitable for preparing a high-viscous solution because of the difficulty of crystallizing out of a supersaturated solution.

Viscosities of these solutions at various concentrations and temperatures were measured by the falling-sphere method. The capillary method viscosimetry is not applicable on account of their high viscosity. In our case, η was calculated from the time t sec., necessary for a steel ball of radius 0.07875 cm. (D=7.80 g./cm.^{3}) to fall down 15 cm. along the central axis of a liquid column of radius 1.4 cm. and of height 30 cm. Thus, viscosities ranging in 2~600 poises were measured.

Taking these solutions, the author measured the degree of spinnability by the above-stated apparatus. The viscosity of a solution at the time when spinnability first appears is thus known.

In this way, the following conclusion was drawn out.

A solution of any concentration generally begins to exhibit spinnability at a temperature at which viscosity amounts to 40~50 poises; in other words, at least 40~50 poises of viscosity are necessary for a simple high-viscous liquid to produce spinnability. This critical viscosity is 4000~5000 times as large as the viscosity of water.

It should however be noticed that, as will be stated below, typically spinnable liquids exhibit marked spinnability at the viscosity far lower than this.

(C) Spinnability of raw rubber solutions.—Solutions of raw rubber in xylene, toluene, and benzene etc. are, as egg-white and saliva, typically spinnable. Using the above-mentioned apparatus, spinnability (expressed by the maximum thread-length, L cm. before breaking) of a raw rubber—xylene solution at various concentrations was measured, by changing a lifting velocity, v of the rod R (*cf.* Fig. 4). As is clear from Fig. 4, spinnability—concentration relation has a maximum, showing that the 3~4%

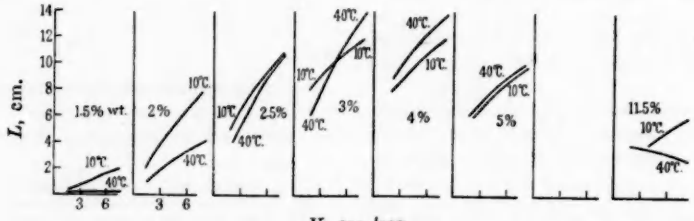


Fig. 4.

solutions exhibit the most remarkable spinnability. This result may be explained as follows by a concept of relaxation phenomenon. Spinnability increases with the increase of concentration or viscosity, but with too much increase of viscosity, a liquid becomes too rigid to follow the testing rod rising upwards with the velocity of several cm. per second, and the breaking occurs: in other words, spinnability is maximum when the time of relaxation of the solution is optimum in comparison with the time of observation or velocity of measurement. Optimum concentration, or the maximum in the concentration—spinnability curve thus takes place.

In marked contrast with sucrose solution in which at least 40~50 poises of viscosity are necessary for it to exhibit spinnability, raw rubber solution, as illustrated in Fig. 4, shows marked spinnability even at 2 poises corresponding to a concentration of 2%. Saliva is also said to have obvious spinnability in spite of viscosity less than 1 poise. The foresight of Jochims,[2] Erbring[3] etc. seems to be correct, for they sought to attribute the remarkable spinnability of such typical spinnable liquids of comparatively low viscosity to a sort of "elasticity" coexisting with viscosity. The concept that spinnability is a co-operation of "viscous flow" streaming down from the tip of a rod and "elastic deformation" analogous to the elongation of a rubber string, appears to be correct.

Anomalous Viscosity (Structural Viscosity)

(A) Anomalous Viscosity. — Non-Newtonian flow is characteristic of most colloidal solutions, especially lyophile ones. In these cases, viscosity η is not a constant independent of shearing stress of flow, but generally decreases with the increase of the velocity gradient. The so-called Hagen-Poiseuille's law in the capillary flow does not hold.

When the Newtonian liquids are made to flow through a capillary of radius r and length L by means of a pressure p, and a volume v of fluid passes through it in a time t_0 sec., then viscosity η of a liquid is according to Hagen-Poiseuille's law

$$\eta = \frac{\pi p r^4 t_0}{8vL} = \text{const.} \times pt_0 \qquad (1)$$

(provided v=const.)

In the ordinary Newtonian liquids, η or pt_0 is independent of p. In most of lyophile colloidal solutions, on the other hand, pt_0 is not independent of p, but generally decreases with the increase of p. Wo. Ostwald ascribed this effect to the destruction of an internal structure by the shearing stress of flow, and called it "structural viscosity"; but strictly, this effect might not always be attributed to this sole mechanism, and it will be rather safe simply to say anomalous viscosity or non-Newtonian flow (*cf.* Fig. 5).

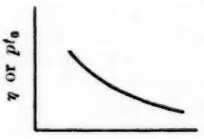


Fig. 5.

Philippoff[4] assumed a sort of elasticity in the non-Newtonian colloidal liquids, and presented the following formula,

$$\left.\begin{aligned} \eta^* &= \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + 2P_R^2/(3G^2)} \\ P_R &= rp/(2L) \end{aligned}\right\} \qquad (2)$$

where η^* is the apparent viscosity gained from Eq. (1) into which we insert the experimental data mechanically (though, strictly speaking, it is nonsense to use Eq. (1) for non-Newtonian liquids). P_R means the shearing stress at the wall of a capillary, whose radius and length are r cm. and L cm. respectively, when pressure p dyne/cm.^{2} is given on the end of a capillary; this is also a formal diversion of the relation which holds only in the Newtonian flow, in which shearing stress changes linearly from zero at the central axis of a capillary to a maximum value at the wall of it as is given by the under formula of Eq. (2). η_0 and η_∞ are constants and correspond to $[\eta^*]_{P_R \to 0}$ and $[\eta^*]_{P_R \to \infty}$ respectively. G is a coefficient of the so-called fluid-elasticity, and in the case of the capillary flow, means a torsional elastic constant or rigidity. Thus, if we adopt the standpoint of Philippoff, it is possible to estimate the magnitude of an elastic constant of a sol by means of an experimental η^*—P_R curve.

(B) Anomalous Viscosity of the Spinnable Solutions.—The author studied elasticity of the typically spinnable liquids following Philippoff.

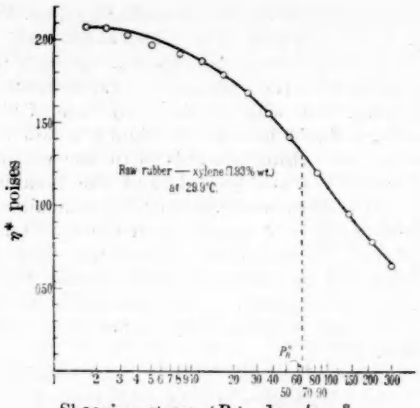
Since η must be plotted as a function of pressure p, the common Ostwald's viscometer

(4) W. Philippoff, *Koll. Z.*, **71**, 1 (1935); *ibid.*, **75**, 142, 155 (1936); *ibid.*, **83**, 163 (1938).

is inapplicable. As the most suitable type for such experiments, the author used Tsuda's horizontal capillary viscometer.[5] A voluntarily changeable pressure p is applied from the two large glass vessels which are connected to each other and each is filled with a certain amount of water, and then p equals the difference of the water-head of the two vessels.

Strictly speaking, all capillary type viscometers are in principle improper for the study of anomalous viscosity, because, in the capillary flow, the shearing stress P varies with the radial distance from the center of a capillary, so that the shearing stress at the wall is maximum and is zero at the center of a tube. This fact is not consistent with our aim to know η in relation to the shearing stress P. Couette's rotational viscometer is the most rational, for in this case the shearing stress P is almost constant, independent of the radial distance as long as the gap between the two cylinders is small as compared with radii of the two cylinders. Nevertheless Tsuda's horizontal capillary viscometer is preferable to the rotation type from the practical point of view; the latter is accompanied with some faults, namely, the structural complexity and the difficulty in controlling temperature.

Experimental results on anomalous viscosity of xylene solution of raw rubber ("pale sheet") are illustrated in Fig. 6 and Fig. 7. For reference, the η^*—P_R curves for sucrose solution aq. and vanadium pentoxide sol are added in Fig. 6. Take three sets of (η^*, P_R) values, then from Eq. (2) three constants G, η_0 and η_∞ can be determined. Using, for example, from the lower curve about raw rubber—xylene system in Fig. 6, the following three points



Shearing stress (P_R), dyn./cm.²

Fig. 7.

$$\begin{cases} \text{A } (P_R = 2.43, & \eta^* = 0.933), \\ \text{B } (P_R = 17.2, & \eta^* = 0.791), \\ \text{C } (P_R = 85.6, & \eta^* = 0.497), \end{cases}$$

we obtain

$$G = 21.6 \text{ dyn./cm.}^2, \qquad \eta_0 = 0.935 \text{ poise}$$
$$\eta_\infty = 0.450 \text{ poise}$$

Or, since the inflection point of Eq. (2) can be determined from the condition

$$\frac{d^2\eta^*}{dP_R^2} = 0, \qquad (3)$$

it is obtained from Eq. (2) and Eq. (3), the next formula, provided P_R^* means a value of P_R at the inflection point.[4]

$$G = \sqrt{\frac{2}{3}} P_R^* = 0.815\, P_R^*$$

Using, for example, $P_R^* = 60 \sim 70$ from Fig. 7,

$$G \fallingdotseq 50 \text{ dyn./cm.}^2$$

This is another procedure of determining G.

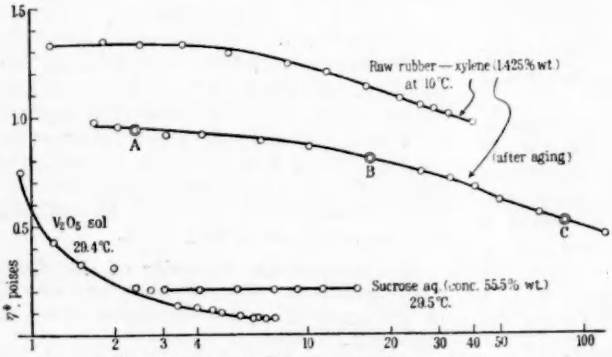
Maxwell's classical formula relating the time of mechanical relaxation λ

$$\lambda = \eta / G$$

becomes

$$\lambda = \eta_0 / G$$

in the case of Philippoff's formulation of anomalous viscosity. From the above-gained



Shearing stress (P_R), dyn./cm.² ($=rp/(2L)$)

Fig. 6.

(5) S. Tsuda, *Koll.-Z.*, **45**, 325 (1928); Wo. Ostwald and H. Malss, *Koll.-Z.*, **63**, 61 (1933).

$\eta_0 = 0.935$, $G = 21.6$,

$$\lambda \fallingdotseq 0.04 \text{ sec.}$$

Since, on the other hand, our observation time, when we speak of the appearance of spinnability, is supposed to be 0.1～1 sec., the rubber solution of such a low concentration (1.5%) has a relaxation time much less than our observation time. Accordingly, the tendency to flow down is much stronger than the tendency to elongate to a liquid-thread, so that spinnability is not yet remarkable, as illustrated above (Fig. 4). However, as will be discussed later again in Part II, in a 3～4% rubber solution λ becomes the order of 0.5 sec., so that marked spinnability is observed on account of the fact that the relaxation time λ is comparable with our observation time. With the increase of the concentration moreover, λ of the fluid becomes presumably far larger than the observation time t. This situation, that the deformation of fluid can not follow the testing velocity, results in the snapping or breaking of a thread rather than extending or elongating it; spinnability decreases in this way (*cf.* Fig. 4).

Summary

Simple viscous liquids become thread-forming first at the viscosity of 40～50 poises or more.

Spinnability of typical thread-forming liquids is characterized by the co-operation of the far smaller viscosity and some "elasticity."

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

Spinnability of Liquid. A Visco-elastic State. II. Spinnability and Visco-elastic Property

By Tsurutaro NAKAGAWA

(Received November 2, 1951)

Spinnability as a Visco-elastic State

From the statements and examples in the previous paper, it seems to be almost admissible that a sort of "elasticity" accompanying the thread-forming liquids is an important factor of the spinnability phenomenon. As was stated above, by analysing the η^*—P_R curves of anomalous-viscous liquids exhibiting spinnability, we estimated the value of the elastic constant specifying that elasticity, and assumed it to be probable that spinnability is a co-operation of a viscous flow specified by a relatively small coefficient of viscosity ($\eta = 10^0 \sim 10^1$) on the one hand, and an elastic deformation corresponding to a coefficient of elasticity $G = 10^1 \sim 10^2$ on the other hand. But the determination of G by the analysis of anomalous viscosity is an indirect way, and it will not always be permissible to use Philippoff's equation without any reservation. As was mentioned already, the elasticity of spinnable liquids is not a theoretical parameter, but a physical reality which is actually observed. When a liquid thread snaps, it springs back elastically; or when these liquids are left free after a violent agitation, an elastic returning in the liquid actually occurs.

Is a direct measurement of such elasticity impossible? In our case, as is easily understood, the usual statical methods, namely, the methods of observing a static elastic equilibrium between stress and strain are inapplicable because of a marked relaxation or a flowing which accompanies an elastic deformation. The author designed thereupon the following dynamic method, in which is observed a mechanical resonance of a body which is oscillated by an oscillatory force transmitted through a torsion wire and is suffering, from a surrounding liquid, viscous resistance proportional to the deformation velocity and elastic resistance proportional to the deformation rate.

Principle of the Method for a Measurement of Visco-elastic Constants —Forced Oscillation Resonance Method

Consider a device as is illustrated in Fig. 1.[1] We shall discuss the motion of the inner cylinder when it is forced into oscillation through a torsion wire. The sinusoidal rotational displacement

$$\Theta(t)=\Theta_0 \sin \omega t$$

$(\omega=2\pi\nu;\ \nu;$ frequency$)$

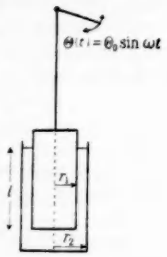


Fig. 1.

is given at the upper end of the torsion wire. The space between the inner and the outer cylinder is filled by a visco-elastic liquid.

Then

(inertial resistance of the cylinder)+(viscous resistance of the liquid)+(elastic resistance of the liquid)=(external elastic force from the torsion wire)

where

$$(\text{inertial resistance})=I\ddot{\theta}$$

I: moment of inertia of the inner cylinder

$$(\text{viscous resistance})=R_1\dot{\theta}$$

$$(\text{elastic resistance})=E_1\theta$$

$$(\text{external force})=k(\Theta-\theta)$$

k: torsion constant of the torsion wire

Therefore, the equation of motion of the inner cylinder is

$$I\ddot{\theta}+R_1\dot{\theta}+E_1\theta=k(\Theta-\theta) \qquad (1)$$

or

$$\ddot{\theta}+2\varepsilon\dot{\theta}+n_e^2\theta=L\sin\omega t \qquad (2)$$

where, $2\varepsilon\equiv R_1/I$

$n_e^2\equiv(k+E_1)/I$

$L\equiv k\Theta_0/I$

Since the transient term of the general solution of Eq. (2) damps soon, the singular solution is sufficient as long as we are concerned with a stationary state when the observation is made. The stationary state solution, therefore, is

$$\theta=\frac{L}{\sqrt{(n_e^2-\omega^2)^2+4\varepsilon^2\omega^2}}\sin(\omega t-\phi)$$

$$\equiv A\sin(\omega t-\phi) \qquad (3)$$

where, $\tan\phi=2\varepsilon\omega/(n_e^2-\omega^2)$

The amplitude of the forced oscillation of the inner cylinder is, therefore,

$$A=\frac{L}{\sqrt{(n_e^2-\omega^2)^2+4\varepsilon^2\omega^2}}\equiv L/\sqrt{f(\omega)} \qquad (4)$$

Condition of the amplitude resonance is

$$A=\max. \quad \text{or} \quad f(\omega)=\min.$$

namely $\dfrac{\partial A}{\partial\omega}=0$ or $\dfrac{\partial f}{\partial\omega}=0$

Calculation of this gives

$$\omega_{res}^2=n_e^2-2\varepsilon^2, \quad \text{or} \quad \nu_{res}=\frac{1}{2\pi}\sqrt{n_e^2-2\varepsilon^2} \qquad (5)$$

where ω_{res} and ν_{res} mean ω and ν at resonance respectively, and consequently

$$A_{res}=L/\sqrt{4\varepsilon^4+4\varepsilon^2\omega_{res}^2} \qquad (6)$$

where A_{res} means A when resonance.

If, therefore, A_{res} and ω_{res} are observed, ε and n_e are calculated from Eq. (6) and Eq. (5), so that R_1 and E_1 are known from Eq. (2).

We have, on the other hand, the next two relations[2],[3]

$$\begin{cases}\eta=\dfrac{R_1}{4\pi l}\left(\dfrac{1}{r_1^2}-\dfrac{1}{r_2^2}\right) & \text{poises}\\ G=\dfrac{E_1}{4\pi l}\left(\dfrac{1}{r_1^2}-\dfrac{1}{r_2^2}\right) & \text{dyn./cm.}^2\end{cases}$$

where η and G are the viscosity coefficient and the elasticity coefficient (rigidity, here) respectively of the fluid between the two cylinders, and r_1 and r_2 are radii of the inner and the outer cylinder respectively, l being an immersion depth of the inner cylinder.

Description of the Apparatus

An apparatus as is illustrated in Fig. 2 was constructed. A rotating disc A and another disc B which oscillates rotationally are connected to each other by a connecting rod R. R is combined to A by a pin; A is provided with several holes

(1) *Cf.* T. Kuyama. "*Kagaku*" (*Science*), **16**, 149 (1946); J. R. Van Wazer and H. Goldberg, *J. Appl. Phys.*, **18**, 207 (1947); T. Nakagawa, "*Kagaku*" (*Science*), **20**, 327, 469 (1950); T. Nakagawa, *J. Chem. Soc. Japan*, **72**, 759 (1951); T. Nakagawa, This Bulletin, **24**, 191 (1951).

(2) E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928.

(3) Th. Schwedoff, *J. de Phys.*, [2] **8**, 341 (1889).

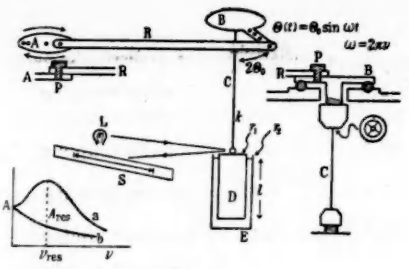


Fig. 2.

which are bored eccentrically at a distance of several millimeters to several centimeters from the center of the disc A, and is pinned by P to R by a certain suitable hole. The B—R coupling is made in a similar way by the holes bored eccentrically at the points several mm. to several cm. distant from the center of B, by using a pin P. A and B are both brass disc plates, 5~10cm. dia. and 5 mm.~1 cm. thick, R being also a brass square rod about 1 meter long. P are brass pins about 4 mm. dia. The under side of the disc B, as is shown in Fig. 2, is provided with a ball bearing to smooth its rotational oscillation. The upper and lower ends of the torsion wire C are each connected to the other body by a chuck whose head is divided in four (*cf.* Fig. 2). If the eccentricity at the A—R coupling is several millimeters, the one at the B—R coupling is several centimeters, and the length of R is about one meter, the rotational angular oscillation of B may be supposed to be almost perfectly sinusoidal. The torsion wire C is a properly selected piano wire, about 0.5 mm. dia. and about 30 cm. long. The inner cylinder D is a glass tube about 5 cm. dia. which is at the upper opening provided with a hard rubber plug to which is attached the above-stated chuck at the center, to be connected to the wire C, and this tube is filled with a proper amount of lead shot to prevent floating up on the one hand and to control the moment of inertia I on the other hand. Since ordinary piano wire has a habit of being bent, it is necessary to straighten it by giving an appreciable weight to D. The outer cylinder E is also a glass vessel about 6.5 cm. dia.

At the chuck which is the lowest end of the wire C, is attached a small galvanometer mirror which reflects a light from a lamp L onto the scale S, and we are able to observe the amplitude of rotational oscillation of D. It should be remembered here that the angle swept by light is double the actual angle of a deflection of the mirror or the body D. The disc A is driven by a phonograph motor, which is convenient to control the revolution speed.

Torsion constant k of the wire C is determined as follows from the observation of a natural frequency or a period T sec. of the free oscillation when a weight of a known moment of inertia I_{kn} is used in place of D.

$$k = 4\pi^2 \frac{I_{kn}}{T^2}$$

As a weight of a known moment of inertia, the author used a brass cylinder of several cm. dia. and height, whose moment of inertia is easily calculated by the formula

$$I = \frac{1}{2} Mr^2$$

(according to the rotation about the longitudinal axis)

where M and r are mass and radius of the cylinder respectively. It is recommended that several of these standard weights of various dimensions be prepared for the sake of calibrating a wide range of magnitude of torsion constant k. The standard weight, too, is provided with an above-stated fastening chuck to be easily connected to the wire. One of them, for example, which we used, has a value of $I = 1.96 \times 10^3$ g. cm.^{2} ($M = 791.2$ g., $r = 2.23$ cm.).

With k thus determined, we are able to know the moment of inertia I of the inner cylinder D, by observing a period T sec. of its free oscillation, according to the formula

$$I = \frac{kT^2}{4\pi^2}$$

The procedure of the observation is as follows. A liquid to test is placed between D and E, and a dipping l is properly controlled. Oscillation is started. Inspecting the amplitude of a light spot on S, we vary a revolution speed of the motor or A, and consequently a frequency of oscillation of B. (In the case of a phonograph motor, we can easily perform this procedure by an accessory speed controlling arm.) As is shown in the curve (a) of Fig. 2, at a certain value of a frequency, the amplitude of the motion of D reaches a maximum which is of course greater than the amplitude of the driving disc B; in other words, a mechanical resonance of D occurs. Record the resonance frequency ν_{res} and the amplitude of a light spot on S at resonance. Then the above-mentioned analysis gives us the values of η and G of the sample; the amplitude of a light spot on S must be of course reduced to the value of the actual angular amplitude A_{res} of D. It must be remembered that when the dipping l, accordingly R_1, is too large, a maximum of the amplitude does not appear (*cf.* case (b) of Fig. 2).

Measurements were carried out under the following condition.

$k = 1.89 \times 10^4$ dyn·cm.

I (of the inner cylinder) $= 1.225 \times 10^3$ g. cm.^{2}

$\theta_0 \fallingdotseq 0.1$ radian

$r_1 = 2.4$ cm., $r_2 = 3.3$ cm.

$l =$ several cm.

The frequency of the free oscillation (for the determination of k or I), and the resonance frequency ν_{res} were all in the neighbourhood of

Table 1

Substance	Spinnability, cm.	η, poises	G, dyn./cm.^{2}	Conc., % wt.	Remarks
Rubber-xylene (I)	4.5	9.3	6.3		series coupling
Rubber-xylene (II)	11.0	51.	105.	3.6	series coupling
Extract of root of *Hibiscus Manihot* L.	1.0	11.3	27.6	2.9	series coupling
Hg sulphosalicylic acid aq. soln. (I)	5.5	4.2	27.8	4.2	series coupling
Hg sulphosalicylic acid aq. soln. (II)	4.5	4.2	35.0	3.1	series coupling
Starch paste	0	5.5	40.0		parallel coupling
Sucrose aq. soln.	0	11.9	0	68.	purely viscous
Water glass aq. soln.	0	16.6	0	61.	purely viscous

1 cycle per second. The resonance amplitude A_{res} was about 0.2 radian.

Experimental Results

In this way, Table 1 was acquired. As is seen in the table, the Newtonian liquids as a sucrose solution and a water glass solution do not exhibit spinnability even at the comparatively higher viscosities; that these purely viscous liquids require viscosity of 40~50 poises or more to become thread-forming, was already stated. Typically thread-forming liquids, on the other hand, as a rubber solution, an extract of a root of *Hibiscus Manihot* L., a solution of mercury sulphosalicylic acid etc. possess marked elasticity besides relatively low viscosity as is read in the table. Such co-operation of a simple viscous flow and an elastic deformation is responsible for the typical spinnability phenomenon. A thread-forming state is an elastic deformation like the elongation of a rubber string, superposed upon a viscous flow streaming down from above. This elastic deformation, however, is one which corresponds to a relatively small λ, time of relaxation. When this relaxation time is in the same order as our observation time t (0.1~1 sec.) at the spinnability test, displacement is nearly elastic (reversible). But for a test of a sufficiently long period the displacement becomes viscous (irreversible). So that even in the typically spinnable liquids spinnability does not appear when they are treated by means of a very slow observation speed; a liquid thread will not be formed when a rod is raised up too slowly from a liquid.

Starch paste exhibits no spinnability in spite of its typically visco-elastic nature; this fact will be discussed later.

Spinnability (cm.), as was already described in the paper I, means the maximum length of the liquid thread spun between the surface of the liquid and the tip of the ascending rod, which is an arbitrary measure of the thread-forming ability of a liquid.

Discussions

(A) Optimum Values of η and G for Spinnability.—We have thus an idea that spinnability or the thread-forming property of some liquids is a superposition of a simple viscous flow and an elastic deformation, and determined experimentally the value of a viscosity coefficient specifying the degree of flowing and an elasticity coefficient specifying the extent of an elastic deformation. Now the next problem is to know the optimum values of η and G for thread-forming liquids to exhibit the most remarkable spinnability. To estimate these values, the author experimented as follows.

As is shown in Fig. 4 of Part I, spinnability of a raw rubber—xylene solution has a maximum at a concentration of 3~4% by weight. Direct measurement of viscous elasticity of a 3.6% solution gives the following values (*cf.* Table 1)

$$\eta = 51 \text{ poises}, \quad G = 105 \text{ dyn./cm.}^2$$

These values will presumably indicate the order of the optimum values for spinnability. According to Maxwell's relation, the time of mechanical relaxation λ is

$$\lambda = \eta/G \fallingdotseq 0.5 \text{ sec.}$$

This value of λ is just the same order of the time-scale t of our experimental investigation or the experimenting speed when we test the existence of spinnability. That the mechanical relaxation velocity of a system just coincides with the testing velocity, is a necessary condition for the appearance of the most remarkable spinnability. The case stated here just satisfies this condition.

(B) The Problem of the Coupling Type of η and G.—As was referred to previously, starch paste, a typical visco-elastic substance, does not exhibit spinnability. How is it explained?

The behavior of a material exhibiting a flow superimposed upon elasticity can be represented by means of mechanical models as follows (*cf.*

Fig. 3).[4],[5] Here the elastic mode of response to stress is indicated by a "spring", and the flow mechanism by a "dashpot" in which a

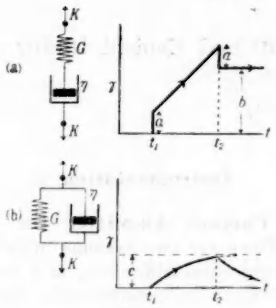


Fig. 3.

porous piston is assumed to move in viscous fluid. If stress is imposed, the ends can move either by a stretching of the spring, or by a flow in the dashpot. The response of the material to a stress can, in this way, be translated into the corresponding behavior of the mechanical model. As the simplest of such models of viscous elasticity, the next two types, as is illustrated by (a) and (b) of Fig. 3, are assumed. Take first the model (a). Impose a constant stress K at the ends, and plot the displacement γ against time t, then the behavior of the system will be as shown in the right-hand diagram of (a). When the stress K is applied at the time t_1, the spring instantaneously stretches to the amount a corresponding to (K/G), and at the time the dashpot begins to elongate steadily at the rate (K/η). When the stress K is removed at the time t_2, the spring instantaneously contracts by the amount a, but the dashpot remains in its elongated condition, and the amount of viscous flow b during the time (t_2-t_1) does not recover permanently.

Consider the second case (b). This device differs from that of the case (a) in that the spring and the dashpot are coupled in parallel, not in series. When the stress K is applied at t_1, the elastic stretching of the spring does not occur in phase with the stress, on account of the viscous damping resistance which is coupled in parallel with the spring. The equilibrium position of elastic deformation is reached asymptotically. And, moreover, unlike the case (a), total displacement does not exceed a value c corresponding to (K/G), even if the loading continues forever. When the load is removed at t_2, the ends return completely to the initial position of zero displacement through the same asymptotic path as above. Such a deformation type is called retarded elastic response, and such a time effect is called elastic after-effect.

Now the series mechanical model (a) is fit to symbolize the mechanical behavior of thread-forming fluids, for it is capable of elongating infinitely by a certain stress. The parallel model (b) is a case of a finite elongation for a certain stress, and the attempt to elongate it at a constant speed, seems to produce splitting or breaking into pieces, without forming a thread. When we call the former case (a) the series coupling and the latter (b) the parallel coupling of viscosity and elasticity, the mechanical behavior of starch paste may correspond to the latter *viz.* the parallel type of visco-elasticity.

Summary

According to the experiments and considerations presented above, a mechanical model as Fig. 4 is introduced for the thread-forming state of liquid. The thread-forming state is the "series" coupling of elasticity corresponding to $G=10^0\sim10^2$ dyn./cm.^{2} (some millionth of G for rubber) and viscosity which corresponds to $\eta=10^0\sim10^1$ poises (some thousands times η for water). This is spinnability.

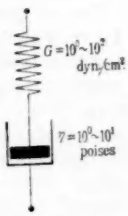


Fig. 4.

The author wishes to express his thanks to Prof. J. Sameshima and Prof. H. Akamatsu for their leadership. The expenses connected with this investigation have been defrayed by the grants from the Ministry of Education, to which his thanks are also due.

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

(4) T. Alfrey, "Mechanical Behavior of High Polymers," Interscience Publishers, New York, 1948.
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Pen Writing Polarograph with Direct Current Amplifier. — Study of *p*-Nitrosodiethylaniline —

By Sinichi KIKUCHI, Yoshikata SAKAGUCHI and Kenichi HONDA

(Received November 12, 1951)

Introduction

It is twenty-six years since polarography was born. There have been many studies of this subject especially in recent years as J. J. Lingane reported in Analytical Chemistry.[1],[2] Excited by the industrial use, the polarographic apparatus has gained remarkable progress and is ready for the new application. According to the progress of the apparatus, it is just now going to break new ground in polarography. The present authors feel keenly the importance of instrumentation for the above-mentioned considerations.

One of the eminent developments is the invention of a pen-writing device without photographic paper. It has been studied chiefly in U. S. A.,[1],[2] but to our disappointment, the structure of those devices has not been described in full.

Two of the present authors—S. Kikuchi and Y. Sakaguchi—employed the direct current amplifier and its recorder for silver potentiometric studies of photographic fog inhibitors,[3],[4],[5] while S. Kikuchi and K. Honda were studying the polarography for the research of the electrolytic preparation of diethylparamine from *p*-nitrosodiethylaniline.[6] The former is known as the developer of color photography.

Here we have combined both techniques, and have obtained excellent polarograms. We have compared the polarograms of *p*-nitrosodiethylaniline obtained with this recorder and those of ordinary photographic apparatus. We should like to report as follows, because we had satisfying results. We wish to write at this opportunity that the second and more improved apparatus is being made now.

Instrumentation

Direct Current Amplifier for Polarograph.—There are two systems which record the small potential difference, as a rule. The one is the recording potentiometer system, and the representative is Sargent visual recording polarograph[1] with Brown Electronik potentiometer recorder. The merits of this system are to keep good equilibrium notwithstanding the variation of voltage of alternating lines and to record with rectangular coordinates in a chart and so to have good reliance. On the other hand its defects are that half-period of the potentiometer is too long as it needs several seconds to cover all the range and the price is considerably expensive—this is an important problem in Japan.

The other is the direct current amplifier and recorder system and the representative is Polaro Analyzer[1] of Rutherford Instrument Co. The merit of this system is that half-period of recorder is within one second. This allows us to use it not only in the industial application, but also for theoretical studies. Among other instruments, this is very cheap, the predominant merit for us. The defects of this system are the use of the direct current amplifier for this purpose is very difficult, and especially difficult, in Japan, because of the bad quality of the electric line in Japan, and that it records with curved coordinates. Considering all these conditions, we adopted the latter.

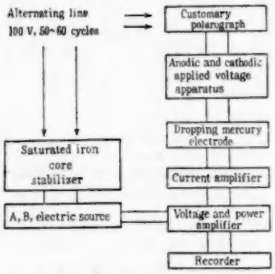

Fig. 1.—Block diagram of pen-writing polarograph with direct current amplifier.

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(3) S. Kikuchi and Y. Sakaguchi, *J. Soc. Sci. Phot. Japan*, **12**, No. 4, 3 (1950).
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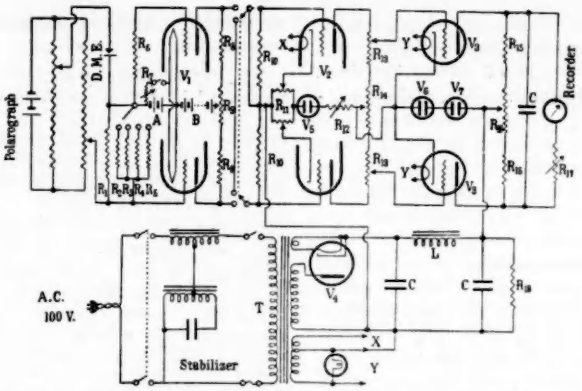


R_1	1	MΩ	R_{13}	50	KΩ V. R.	V_5	VRA 60/80
R_2	1.5	KΩ	R_{14}	20	KΩ V. R.	V_6	VRB 135/60
R_3	2	KΩ	R_{15}	10	KΩ	V_7	VRA 140/50
R_4	3	KΩ	R_{16}	2	KΩ V. R.	A	two of 1.5 volts dry battery (special unit one)
R_5	5	KΩ	R_{17}	5	KΩ V. R.		
R_6	3	KΩ	R_{18}	1	MΩ	B	67.5 v. piled dry battery
R_7	10	Ω variable resistor	C	4	μF oil filled condenser	T	secondary 350 v. 70 mA. 6.3 v. × 2 5 v. for 40 watts
R_8	30	KΩ	L	10	H 80 mA.		
R_9	5	KΩ V. R.	V_1	UZ30MC			
R_{10}	3	MΩ	V_2	US6SL7GT			
R_{11}	100	Ω V. R.	V_3	UY76		D. M. E. dropping mercury electrode	
R_{12}	600	Ω V. R.	V_4	KX80HK		Every resistors are for 1 watt.	

Fig. 2.—Circuit of the amplifier.

Then the amplifier is the main point of this report. The mechanism of this system is shown in Fig. 1 as the block diagram.

When the polarographic current I flows on the resistance R—1.5 KΩ~5 KΩ, the potential drop is IR which is amplified so as one can get the polarograms on the recording milli-ammeter. Suitable voltage amplification degree and power amplification degree to drive the recorder are possessive functions of course. The circuit of this amplifier is shown in Fig. 2.

Balanced type UZ 30 MC preamplifier with dry batteries was made to recover the shortage of amplification degree of main amplifier which had been made to potentiometric titrations. Its voltage gain was about 6 times. The main amplifier based on the balanced bridge of 6SL7GT and two of UY76 was a eliminator system and its voltage gain was about forty times, in other words it needed 400 mv. for a full swing of the recorder.

Stability of the amplifier was obtained by the next three methods. The first was the customary saturated iron core type stabilizer; the second was "μ balanced circuit"[7] which was composed of R_{11}, V_5, and R_{12} in 6SL7GT's circuit; the third was stabilo-volt tubes of V_6 and V_7 in UY 76's circuit. The "μ balanced circuit" is as follows,

$$\mu = (-dE_p/dE_g)_{I_p}$$

where, μ is amplification factor, I_p is plate current E_p is plate voltage, and E_g is grid voltage. Controlling that $-dE_p/dE_g$ is equal to μ of the tube, one gets the constancy of plate current. It is that $1/\mu$ of dE_p is negatively fed back to the grid. The stabilo-volt tube is used for taking formulated ratio. If it is fed back to slightly excess, it is possible for one to avoid the variation of emission of

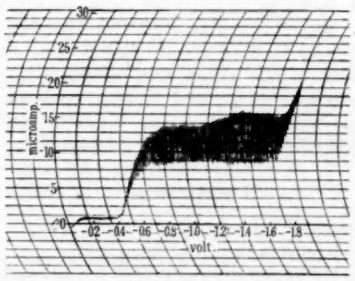


Fig. 3.—Micro-ampere and voltage graduation of the co-ordinates with the example of the polarogram by the amplifying method.

(7) G. P. Harnwell and S. N. Van Voorhis, *Rev. Sci. Instruments*, **5**, 244 (1934).

filament. Thus, the movement of zero-point of this direct current amplifier was within 1% between 90 and 110 volts of alternating lines.

Having combined pre-amplifier, main amplifier, and recorder, the micro-ampere and voltage graduation was shown in Fig. 3 where in-put resistance was 2KΩ.

Its stability was a function of A dry battery, which was able to be employed about five hours. The movement of zero-point was 3% of full range in fifteen minutes. B battery was not changed. The total error of this recording system was within 5%. The amplification degree was adjusted by R_2, R_3, R_4, R_5, and R_{17}: and zero-point was adjusted by R_9 and R_{14} roughly, and by R_{16} finely. The main amplifier was originally a voltage amplifier, then the potential difference of anode pool electrode *vs.* calomel electrode was recorded with this amplifier. The graduation in the chart on this case was as shown in Fig. 4.

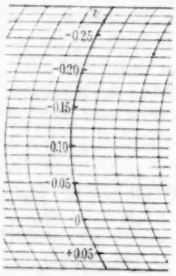


Fig. 4.—Voltage graduation of the anode potential *vs.* S. C. E.

There were four combinations of electric source, stabilizer, and main amplifier. Only one or two of them were suitable for good recording; then the combination was changed occasionally by inspection. The apparatus was not electrically grounded.

Recorder.—It was a direct current 2 milliamp. recorder and its inside resistance was 6000 Ω and its half-period was within one second. It had twelve chart speeds, but we used usually that of 20 mm./min. The effective width of the chart was twelve cm. and its length was 20 m., and it was moved with a clock. This recorder was made by Yokogawa Electric Works, Japan, in 1951.

Experimental

As described before, *p*-nitrosodiethylaniline was studied polarographically, using both our new pen-writing apparatus and ordinary photographic apparatus. The aim is to test the faculty of this new apparatus by comparing the data gained from both apparatuses and so to contribute to the study of electrolytic reduction of *p*-nitrosodiethylaniline.

(a) **Preparation.**—*p*-Nitrosodiethylaniline investigated here, was synthetized from diethylaniline and sodium nitrite,[8] and further recrystallized twice as dark green needles from methanol. Its m. p. was 84.5~85°C. This compound was dissolved in ethanol to the concentration of $5\cdot10^{-3}$ mol/l. as the stock solution. On the other hand, Sϕrensen's citrate-HCl, citrate-NaOH, borate-HCl, and borate-NaOH buffer solutions were prepared, which, were added to the stock solution with the ratio of 4:1~40:1 to make up the proper concentration of test solution. The electrolysis was carried out with the anode of mercury pool at the constant temperature of 20°C. in the liquid paraffin bath. The potential of the anode was measured with potentiometer or amplifying recorder referring to the saturated KCl calomel electrode after each electrolysis. The drop time of capillary was 5.7 sec. per drop and the value of $m^{2/3}t^{1/6}$ was found to be 1.8 mg.$^{2/3}$ sec.$^{-1/2}$ in water with no applied potential. To remove oxygen from the solution, nitrogen was bubbled. As for the photographic polarograms, they were recorded using Yanagimoto's pre-war type polarograph.

(b) **Results.**—*p*-Nitrosodiethylaniline gives only one typical reduction wave and its limiting current is very clear. The values of the half-wave potentials of this in buffered ethanol solution *vs.* various *p*H values, and also the values of the wave heights in the same solution at the concentration of 10^{-3} *M./*l., are tabulated in Table 1. In this table, the half-wave potentials obtained by amplifying method which adopts the inserted resistance of 2 KΩ, and those of photographic are compared. The wave-heights in the table are measured from the polarograms by the former.

Table 1

Comparison of Half-wave Potential *vs.* *p*H by Both Methods. Concentration of the sample is 10^{-3} *M./*l.

*p*H	$E_{1/2}$ v. (v. s. c.)		Wave height, microamp.
	pen-writing	photographic	pen-writing
1.93	+0.124		
3.36		+0.053	
4.16	−0.008	−0.031	6.9
5.98	−0.128	−0.229	6.6
7.93	−0.272	−0.287	6.0
9.91	−0.583	−0.598	6.1
11.7	−0.559		7.2

Inspecting this table, the differences between the $E_{1/2}$ of both methods are about 10 mv. with one exception. The present authors think that possible fluctuation of $E_{1/2}$ which often appears in the irreversible system of such organic compounds, can actually make this difference negligible, and consequently the potential drop by the

(8) Kopp, *Ber.*, **8**, 621 (1875).

inserted resistance which is $2 \cdot 10^3 \, 2 \times 6 \cdot 10^{-6}$ amp. $= 12$ mv. in this case, becomes not very important.

Now going back to the standpoint of polarographic study, it is concluded that the reduction mechanism would be the same in the whole pH range because of the similar wave form and the character of each polarogram. The half-wave potential of this compound is more positive than those of other nitro compounds and so it shows that this compound is very easily reducible. This corresponds to the results of the former investigation about electrolytic reduction.[6] Especially, in the solution of pH value 1, the reduction proceeds with no applied potential.

The relation between the $E_{1/2}$ and pH shows their complete linearity over the whole pH range with one exception which seems to be the experimental error. The increase of $E_{1/2}$ per unit pH value is about 75 mv.

The relation of concentration and wave height at the pH 9.91, in the case of using the amplifying method is shown in Table 2. It shows their linearity generally, between the range of 2.5×10^{-4} and 3×10^{-3} M./l.. From this result, it is proved that this pen-writing apparatus can be used especially for quick quantitative analysis.

Table 2

Relation between Concentration and Wave-height (pH = 9.91)

Concentration, M/l.	Wave-height, micro amp.
2.5×10^{-4}	1.88
5×10^{-4}	3.13
1×10^{-3}	6.72
2×10^{-3}	10.0
3×10^{-3}	15.6

Summary

A new type of polarographic apparatus which utilizes the amplifying method and recorder is described. And its faculty is studied by comparing it with usual photographic apparatus. At the same time, p-nitrosodiethylaniline is studied polarographically and the comparison of both apparatuses is achieved through that study.

Laboratory of Electrochemistry and Photochemistry, Institute of Industrial Science, Tokyo University, Chiba.

Studies on the Gas-Liquid Interface by Surface Potential Measurements III. The Surface Aging of the Solutions of the Long-chain Dibasic Acids

Hiroshi HOTTA and Toshizo ISEMURA

(Received September 13, 1951)

When a new surface is formed on the top of a solution by sweeping the surface with a glass barrier, the solute in the solution will begin immediately to be adsorbed on the freshly formed surface. The rate of adsorption depends mainly on the nature of the solute if the other conditions are the same, and is a problem of some interest in regard to the structure of the layer and the mechanism of adsorption. The adsorption equilibrium of polar organic compounds on the surface of its solution can be considered as a result of competition of the hydrophilic nature of polar groups and the hydrophobic nature of the nonpolar part of the amphipathic molecule. In a homologous series the solute of low molecular weight readily reaches a steady state. With the solute of moderate molecular weight, the ormation of a completely adsorbed layer needs considerable time. On the other hand, the solute of high molecular weight requires so much longer time for equilibration, that the solution apparently reaches a steady state immediately. In a homologous series of the amphipathic compounds, it is generally expected that the lower the molecular weight of the solute is, the higher the solubility and the larger the mobility of the solute is.

The variation of a surface layer will be reflected on the surface tension and surface potential of the solution. Hence, the rate of adsorption can be readily followed by measuring the surface tension and the surface potential as a function of time. In the course of our previous investigation,[1] the change of surface

(1) T. Isemura and H. Hotta, *Bull. Chem. Soc. Japan*, **23**, 193 (1950).

potential with time was found with solutions of some ω, ω'-dicarboxylic acids.

In this respect, the measurements of surface tension and surface potential of the solution are the powerful means to study the change of the surface layer of the solution. In order to observe the change of the surface layer and to clarify its cause, we modified the apparatus used in the previous investigation to adapt it for this purpose. The change of the surface tension and the surface potential was determined with some dicarboxylic acids. From such experiments it was concluded that the adsorption may occur in two stages, initial rapid, and later slow adsorption. In our present experiments, the slow adsorption only was studied. The experimental results will be considered on the ground of the kinetic molecular theory.

Experimental

Experimental Methods.—The apparatus used in our present experiment was a combination of a surface balance of hanging plate type and a surface potentiometer of vibrating electrode type. A thick-walled shallow glass trough, $0.7\times7.0\times15.0$ cm. was used for the economy of the solution. The vibrating electrode of the diameter of 20 mm. was hung over the middle of the trough and the glass plate for the surface tension measurement was inserted into the solution by the side of the electrode. The other electrode made of platinum wire was immersed over-night in the same solution prior to the experiment by using such a syphon as shown in Fig. 1. In order to observe the surface aging of the solution, the surface of the solution was cleaned before starting by the paraffined glass barrier.

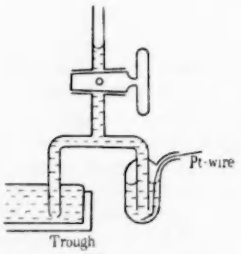


Fig. 1.

The amplifier of the surface potentiometer consists of two parts, *i. e.*, the pre- and main amplifier. The main amplifier is a three-stage tuned amplifier for *ca.* 500 c./s. using three CZ-501 D tubes.

The change of the surface tension was followed by the hanging plate method, and the displacement of the plate was measured by an optical lever.

The level of the surface of the solution was defined by using a telescope.

The materials used in the present experiment were adipic, suberic, azelaic, sebacic and γ,γ'-sulfonyl dibutyric acid. Most of the measurements were made with acidulated solution by hydrochloric acid (in a concentration of 0.015 *N* HCl) if without any special indications. With sebacic acid, a measurement was also made for comparison with aqueous solution. The monolayer of ω,ω'-hexadecadicarboxylic acid was also studied by the technique generally used for insoluble monolayer. All measurements were made at room temperature in a small closed chamber without any special temperature regulation. However, the variation of temperature in the course of measurement to obtain a single curve never exceeded more than 0.4°. At first, it was confirmed that the change of surface tension of pure water with time was not detectable during a course of experiment (within 1.5 hours). The effect of evaporation was also negligible in such a small closed chamber.

Results.—From such experiments as the above it was found that the rate of change of the surface tension was generally parallel to that of the surface potential. However, at the last stage of adsorption of the nearly saturated solution of sebacic acid after 60 minutes, both rates were not parallel to each other. (See curves f and f' in Fig. 3 and 4.) In this respect, some theoretical consideration will be given in the following section. No appreciable change of the tension and the potential could be observed with nearly saturated solutions of adipic acid (0.095 mol/l.) and of γ,γ'-sulfonyl dibutyric acid (0.017 mol/l.) at 22°.

A part of the experimental results is shown in the following figures (Fig. 2, 3 and 4). The surface tension of suberic acid solution in the concentration of 4.5×10^{-3} mol/l. changed definitely by *ca.* 0.1 dyn./cm. during the first four minutes, although the change can hardly be recognized from the figure. Azelaic acid solution of 2.7×10^{-3} mol/l. showed the gradual change of the tension until after 93 minutes when the experiment was disrupted. On the other hand, azelaic acid solution of 1.35×10^{-3} mol/l. showed no change. Meanwhile, all the solutions of sebacic acid examined changed the tension even in a concentration as dilute as 1.87×10^{-4} mol/l.

From these results it can be concluded that the shorter the dicarboxylic acid is and the more dilute the solution is, the shorter is the time required for equilibration. In the case of sebacic acid, the surface tension and potential of the most dilute solution showed an appreciable change after a considerable time.

The absolute value of surface tension can hardly be determined by our present method without any uncertainty, even though the level of the surface of the solution was adjusted to

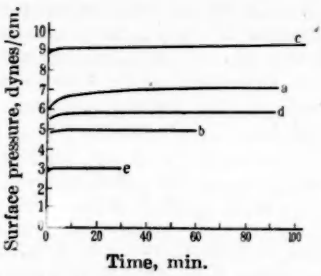


Fig. 2.—The change of surface pressure with time.
(I) Suberic acid solutions in 0.015 *N* HCl: curve a, 9.03×10^{-3} mol/l. (nearly saturated), 22°C.; curve b, 4.5×10^{-3} mol/l., 22°C.
(II) Azeraic acid solutions in 0.015 *N* HCl: curve c, 5.4×10^{-3} mol/l., 20.5°C.; curve d, 2.7×10^{-3} mol/l., 20.5°C.; curve e, 1.35×10^{-3} mol/l., 21.0°C.

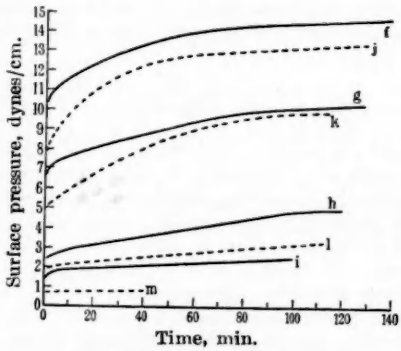


Fig. 3.—The change of surface pressure of sebacic acid solutions with time.—
(I) Solutions in 0.015*N* HCl (full line): curve f, 1.62×10^{-3} mol/l. (saturated), 22°C.; curve g, 8.1×10^{-4} mol/l., 22°C.; curve h, 4×10^{-4} mol/l., 22°C.; curve i, 2×10^{-4} mol/l., 23°C.
(II) Solutions in water (dotted line): curve j, 1.55×10^{-3} mol/l., 22°C.; curve k, 7.7×10^{-4} mol/l., 23°C.; curve l, 3.75×10^{-4} mol/l., 23 °C.; curve m, 1.87×10^{-4} mol/l., 22.5°C.

a fixed level by the aid of a telescope. Moreover, in the initial stage (5-10 seconds) the disturbance of the surface caused by dipping of the plate and the sweeping could not be avoided. However, the rate of surface tension lowering could be determined very accurately. On the other hand, the rate of change of surface potential was also determined quite correctly since we take care of equilibration, sufficiently for this purpose.

In comparison with our previous results,[1] the results on adipic and γ,γ-dibutyl sulphonic acid were in good agreement with previous

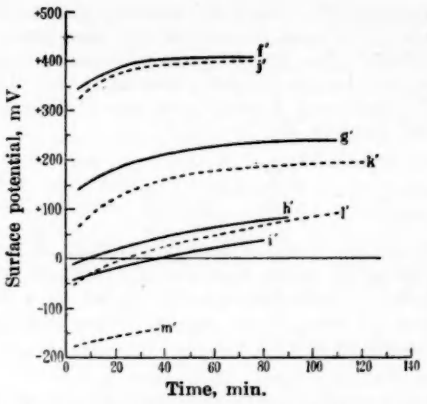


Fig. 4.—The change of surface potential of the sebacic acid solutions with time. Each curve corresponds to that with the same letter without prime in Fig. 3.

ones. The results on other acids showed slight discrepancies. These slight discrepancies may be caused by some fluctuation of the standard potential and by the adsorption of the solute on the electrode dipped in the solution. The electrode in the present experiment was used after equilibration between the solution and the electrode, while the electrode in the previous experiments was used without any such precaution.

ω,ω'-hexadecadicarboxylic acid was examined on 0.1 *N* HCl solution. It gave the film of gaseous type, however considerably deviated from the ideal law. The surface moment of hexadecadicarboxylic acid was determined from surface potential-area relation and was found 0.41 D at the molecular area of 100 Å.², 0.35D at 200 Å.² and 0.32 D at 300 Å.². 0.35 D was used in the later calculation.

Discussion

The mechanism of the change of surface tension with time was recently studied by several investigators. Some of them[2,3,4] considered that the diffusion of the solute was one of the most important factors. In the case of the fast adsorption such as that studied by Addison,[5] the inference might be correct; however, in the case of slow adsorption such as in our present experiments, this is not

(2) A. F. H. Ward and L. Tordai, *J. Chem. Phys.* **14**, 453 (1946).
(3) S. Ross, *J. Am. Chem. Soc.*, **67**, 990 (1945).
(4) C. M. Blair, *J. Chem. Phys.*, **16**, 113 (1948).
(5) C. C. Addison, *J. Chem. Soc.*, **1943**, 535; **1944**, 252; **1945**, 98.

applicable.[6,7] In the latter case the rate of adsorption must be much slower than that of diffusion. The inference was examined quantitatively in the following manner. According to Ward and Tordai,[2] the rate of diffusion will be given by

$$\frac{\partial M}{\partial t} = D\frac{n_0}{\sqrt{\pi Dt}} \qquad (1)$$

where D is the diffusion constant, M the number of solute molecules per cm^2, n_0 the bulk concentration in molecules per cc., t the time in sec. If we assume values approximately as follows,

$$D=10^{-6},\quad n_0=10^{17}\quad t=10^3$$

in relation to our present experiment, it will be obtained from (1)

$$\frac{\partial M}{\partial t}=10^{13}\quad \text{(molecules per cm.}^2\text{ per sec)}.$$

On the other hand we shall estimate the actual rate of adsorption to be 10^9 molecules per cm^2 per sec. from the present experimental results. The reasons for the estimation will be given in a later part of this report. Now we assume the final state of adsorption was reached by passing over an energy barrier which serves as the rate-determining factor. The adsorption was probably pursued through two stages. The first is the fast adsorption which is mainly concerned with diffusion, and the second is the slow adsorption with energy barriers, which are caused probably from dehydration, electrostatic repulsion, reorientation and so on. In our present experiment, only the second stage of adsorption was investigated, since our method did not fit the investigation of such a fast change occurring in the surface as that of the first stage,

In order to study this problem the cage model of a liquid by Fowler and Slater[8] was adopted as the ground. If we consider a sub-layer under the adsorbed monolayer in the surface, the concentration in the sub-layer may be equal to that of the bulk since the diffusion is enough to made up for the loss by adsorption quantitatively. Therefore, if the number of solute molecules in a unit area of a sublayer is n_{sub},

$$n_{sub}=\frac{2Nc\delta}{10^3}$$

where N is the Avogadro's number, c the bulk concentration in mol/l., 2δ the thickness of sub-layer in cm. The total number of collisions per unit time of a given molecule with the cage wall by the thermal agitation can be expressed by

$$\nu=\frac{3}{2\delta}\sqrt{\frac{2RT}{\pi M}}$$

according to them,[8] where M is the molecular weight. Now, if we assume that one-sixth of the total collision is effective to adsorption, the total number of the effective collisions, Z against unit area per unit time, is written by

$$Z=\frac{1}{6}n_{sub}\nu=\frac{Nc}{10^3}\sqrt{\frac{RT}{2\pi M}}. \qquad (2)$$

This result is formally analogous to the formula[9] previously proposed. Therefore, the number of the actually adsorbed molecules, n_{ads}, per unit area per unit time is given by

$$n_{ads}=\frac{Nc}{10^3}\sqrt{\frac{RT}{2\pi M}}e^{-\Delta F^*/RT} \qquad (3)$$

where ΔF^* is the free energy of activation for adsorption. According to the cage theory, of course, the size of the cage of the solute molecule is equal to that of the solvent molecule, and all molecules in a cage have a similar energy distribution with a perfect gas. We assume this first approximation is the case in our present experiment.

On the other hand we can estimate the actual rate of adsorption from the rate of the surface potential change as follows. It is generally accepted that the relation between the surface potential ΔV and the contribution of each adsorbed molecule to it, namely, the effective moment μ of each molecule is expressed by

$$\Delta V=4\pi N_{ads}\mu \qquad (4)$$

where N_{ads} is the number of the adsorbed molecules in a unit area of the surface. Hence

$$\frac{\mathrm{d}\Delta V}{\mathrm{d}t}=4\pi\left(\mu\frac{\mathrm{d}N_{ads}}{\mathrm{d}t}+N_{ads}\frac{\mathrm{d}\mu}{\mathrm{d}t}\right) \qquad (5)$$

If it is assumed as a first approximation that,

$$\frac{\mathrm{d}\mu}{\mathrm{d}t}=0, \qquad (6)$$

that is the orientation of the molecule of ω, ω'-dicarboxylic acid is not changed by

(6) K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939).
(7) A. E. Alexander, *Trans. Faraday Soc.*, **37**. 15 (1941).
(8) Fowler and Slater, *Trans. Faraday Soc.*, **34**, 81 (1938).
(9) Adam, "The Physics and Chemistry of Surfaces", Oxford, 1938, p. 6.

further adsorption, it is obtained from (5)

$$\Delta(\Delta V)=4\pi\mu\Delta N_{ads}=4\pi\mu n_{ads} \qquad (7)$$

where the symbol Δ means the change for a unit time. Therefore, if the magnitude of μ of the suitable standard substance is known, the rate of adsorption can be calculated from (7). There exists some doubt in respect to the validity of the equation (4). However, this may be cancelled by applying the same equation to a standard substance. In the present case, ω, ω'-hexadecadicarboxylic acid was used as the standard substance, which has *ca.* 0.35 Debye unit of μ in monolayer as mentioned above. Although this value may be somewhat smaller than that expected from the data of monocarboxylic acid[10] and μ should be dependent upon the state of the surface, the above value was adopted for the present calculation, and n_{ads} obtained was shown in the Table 1. With this value ΔF^*, the activation free energy of adsorption, can be estimated with (3), which is also listed in the Table 1.

This value of n_{ads} seems to be too large, because the surface energy per molecule is smaller than kT in the lower pressure region from our present result. This contradiction may, probably, be due to the unsuitable estimation of μ. On the other hand, we can at least point out the propriety of the assumptions that (I) all the adsorbed molecules are undissociated in the acidulated solution; and that (II) equation (6) is valid, that is, the contribution of the change of μ of the already adsorbed molecules to $\Delta(\Delta V)$ can be neglected. However these assumptions effect the estimation of ΔF^* by 0.5 Kcal./mol increase even at the highest, but considerable to that of surface energy per molecule. Neverthless n_{ads} should be smaller, consequently ΔF^* larger.

As already pointed out, in the case of the saturated sebacic acid solution (see curves f and f′ in Fig. 3 and 4), the surface potential attained to the stationary state, while the surface pressure was still increasing. This means that in the fairly close-packed film a small increase of packing would produce a marked increase in surface pressure but scarcely any effect on surface potential as interpreted by Alexander.[7]

Also in Fig. 3 and 4 the effect of the hydrochloric acid was examined in comparison with the aqueous solution. It may be noticed that, in the concentrated solution, the equilibrium values of both acidulated and aqueous solution scarcely suffered any effect in spite of the considerable difference in the initial stage, while, in the dilute solution, the considerable difference on the equilibrium value was found. The surface potential of the aqueous solutions was far more negative than of the acidulated solution. This fact can be explained on the

Table 1

Rate and Activation Free Energy of Adsorption

Solute	Curve in figure	Total effective collison number per second	n_{ads} and ΔF^*	Time, min. 10 ~20	20 ~30	30 ~40	40 ~50	50 ~60	60 ~70	70 ~80	80 ~90	90 ~100	100 ~110	110 ~120
Suberic Acid	a	2.6×10^{22}	n_{ads} (10^9/cm^2/sec)	5.7	—	—	4.3		—	—	—	—	—	—
			ΔF^* (kcal./mol)	17.5	—	—	17.8		—	—	—	—	—	—
	b	1.3×10^{22}	n_{ads}	1.7	—	—	—	—	—	—	—	—	—	—
			ΔF^*	17.9	—	—	—	—	—	—	—	—	—	—
Azeraic Acid	c	1.5×10^{22}	n_{ads}			1.6				0.5			—	—
			ΔF^*			18.0				18.5			—	—
	d	7.5×10^{21}	n_{ads}					0.7					—	—
			ΔF^*					18.1					—	—
Sebacic Acid	f	3.9×10^{21}	n_{ads}	25	13	9.5	4.3	1.9	0	—	—	—	—	—
			ΔF^*	15.4	15.7	16.0	16.4	17.0	∞	—	—	—	—	—
	g	2.05×10^{21}	n_{ads}	30	—	15	—	11	—	—	—	2.5	—	2.2
			ΔF^*	15.0	—	15.4	—	15.6	—	—	—	16.5	—	16.6
	h	10^{21}	n_{ads}					11					—	—
			ΔF^*					14.1					—	—
	i	5×10^{20}	n_{ads}					11					—	—
			ΔF^*					13.8					—	—

(10) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A 130**, 270 (1930).

ground that, the dissociation degree at the surface is somewhat larger on the aqueous solution than on the acidulated solution, if the surface concentration is low, while, the difference of dissociation between both solutions disappears, if the surface concentration is high. The effect of acidulation is not so considerable as in the case of soap.[11] This difference is because of the small dissociation constant of the free acid compared with that of soap. This will be further investigated in future for more evidences.

Summary

The surface aging of the solutions of some ω,ω'-dicarboxylic acids was investigated by measuring the surface tension and surface potential, in a function of time. Only the slow adsorption process was studied in the present experiment.

Adipic, suberic, and azelaic acid reached readily an equilibrium. Sebacic acid showed considerable surface aging. The mechanism of adsorption was assumed in the light of kinetic molecular theory, and the free energy of activation for adsorption was calculated. We obtained the free activation energy, 17.5-17.9 Kcal. for suberic acid, 18.0-18.5 Kcal. for azelaic acid and 13.8 Kcal. or more than this for sebacic acid. Free energy of activation for adsorption was increased to some extent with the surface concentration of already adsorbed solute molecules and consequently, for a certain solution, with the surface age.

Thanks are due to Mr. N. Numasaki for his aid in the construction of the amplifier. The authors' sincere thanks are also due to the Ministry of Education for the financial grant.

The Institute of Scientific and Industrial Research, Osaka University, Osaka

(11) G. C. Nutting and F. A. Long, *J. Am. Chem. Soc.*, **63**, 84 (1941).

Identification of Halogens in Organic Compounds by Means of Paper Chromatography[1]

By Toshio ANDO and Shin-ichi ISHII

(Received November 17, 1951)

In order to identify halogens contained in organic compounds, a usual method of qualitative inorganic analysis has been applied to the solutions obtained by decomposition of the compounds. However, such an analysis is somewhat troublesome and needs a considerable amounts of samples. Lederer[2] has recently described a chromatographic method for the separation of inorganic halides on paper with butanol-ammonia as solvent, but the resolution of chloride and bromide especially was not complete, and the instability of composition of the solvent resulting from vaporization of ammonia was also found undesirable.

Now the present authors have developed a method of identifying halogens of organic substances accurately on paper chromatograms, in which a few drops of Lassaigne's solution obtained by decomposing the compounds in the usual way with sodium were developed favorably with a solvent consisting of butanol-picoline. The spots of chloride, bromide, and iodide were then revealed separately as brown coloration of silver sulfide. A spot of iodide could also be located by a characteristic violet coloration of iodine-starch compound.

Experimental Method

Sample.—0.1 *M* solutions of sodium chloride. bromide, and iodide in water and in aqueous sodium hydroxide of 0.5, 1.0, 1.5, and 3.0 *N* in concentration were used at first for the sake of control. Those of sodium cyanide, sodium sulfide, and potassium rhodanate were also used. The organic substances containing halogen which were used were as follows: benzene hexachloride, chloronitrophenol and aniline hydrochloride (both containing Cl and N), dibromocholestanedione,

(1) The present paper was read by one of the authors (S. I.) before the 7th Meeting of this Institute (Nov. 9, 1950) and also before the 4th Annual Meeting of the Chemical Society of Japan in Tokyo University held on April 7, 1951.

(2) M. Lederer, *Science*, **110**, 115 (1949).

bromophenol blue and bromothymol blue (Br and S), ammonium bromocamphorsulfonate (Br, N and S), and diiodotyrosine (I and N), and also some combinations of them.

Decomposition of the organic compounds.—A small quantity of organic halogenocompound was fused with 3~5 parts of metallic sodium, and the mixture was poured into water of 30~40 times the weight of sodium used. 0.01~0.005 cc. of the Lassaigne's solution thus prepared was applied to a strip of paper.

Filter paper.—A strip (1.8×22 cm.) of the Toyo filter paper No. 131 was used. The Toyo filter paper No. 2 was found unsuitable for the present purpose, as it always contained a slight quantity of chloride and the chromatogram obtained on it was not so fine as to distinguish the spots clearly.

Development and revelation.—One-dimensional ascending type of development was adopted in a test-tube (2.5×25 cm.) containing solvent in the bottom.

Solvents used were as follows: (a) butanol-picoline-water (1:1:0.8 V/V), (b) butanol-propanol-water (1:1.1:1 V/V), and (c) butanol-1.5*N* aqueous ammonia (5:1 V/V). Temperatures were given respectively in the foot-notes of the table.

After development and drying, the paper was sprayed with 0.2 *N* aqueous solution of silver nitrate, followed by washing away the excess of silver nitrate twice with 0.1 *N* nitric acid. Then the paper was either sprayed with 0.2 *N* solution of sodium sulfide or exposed to the atmosphere of hydrogen sulfide. The spot of halide was revealed as brown coloration of the resulting silver sulfide.

In a case of iodide, the following method was also used and proved more sensitive than the former: after development the paper was sprayed with 3% aqueous hydrogen peroxide and then with 0.2% aqueous solution of starch. A fine bluish violet spot of iodine-starch appeared instantly.

Results and Discussions

R_F values of various solutions of inorganic halides, sulfide, and rhodanate when developed with butanol-picoline, butanol-propanol, and butanol-ammonia, and also those of halides obtained from organic compounds containing halogens were summarized in the accompanying table.

Chromatograms of aqueous solutions of inorganic halides.—In aqueous solution of sodium chloride, bromide, or iodide, the butanol-picoline system was found most suit-

Table .

R_F Values of Several Halides and Salts Dissolved in Water or Alkaline Solutions of Various Concentrations and Developed with Several Solvents[a]

Developing Solvent	Solution of Sample (0.1 *M*) in	Halide			Other Relating Salt	
		NaCl	NaBr	NaI	Na_2S	KCNS
Butanol-Picoline[b]	Water	0.22§	0.31	0.59	0.03	0.64
	0.5*N*-NaOH	0.19	—	—		
	1*N*-NaOH	0.18	0.28	0.56		
	1.5*N*-NaOH	0.15	—	—		
	3*N*-NaOH	0.10	—	—		
	Decomposition Solutions of Organic Halogenocompounds*	0.19 ±0.02	0.27 ±0.02	0.56 ±0.03		
Butanol-Propanol[c]	Water	0.28	0.32	0.40	0.14	0.48
	0.5*N*-NaOH	0.27	—	—		
	1*N*-NaOH	0.23	0.26	0.34		
	1.5*N*-NaOH	0.21	—	—		
	3*N*-NaOH	0.18	—	—		
Butanol-Ammonia[d]	Water	0.05	0.08	0.14	0.00_6	0.20
	0.5*N*-NaOH	—	—	—		
	1*N*-NaOH	0.05	0.07	0.13_5		
	1.5*N*-NaOH	—	—	—		
	3*N*-NaOH	—	—	—		

(a) By an ascending method. (b) Butanol-picoline-water (1:1:0.8 V/V); picoline was collected between b. p. 120~155° of pyridine base. Developing temperature was 5~10°. (c) Butanol-propanol-water (1:1.1:1 V/V). Temperature was about 25°. (d) Butanol-1.5*N* aqueous ammonia (5:1 V/V). Temperature was about 28°.

* Summarized results were given.

§ KCl and $CaCl_2$ in aqueous solutions gave R_F values of 0.22 and 0.23 respectively, while $CuCl_2$ and HCl those of about 0.38 and 0.40 respectively, forming presumably salts with picoline.

able to resolve the halides.[3] It was also found that, with the same solvent, an elevation of temperature caused a tendency of decreasing in R_F values, while a dilution of the solution caused a tendency of increasing in R_F.

Application of 0.005 cc. of 0.1 *M* solution proved most adequate, yet the spot could be detected even with 0.01 *M* solution.

An aqueous solution of the chloride of potassium or calcium was also developed with the same solvent and was found to show the same R_F value for the chloride. That of cupric chloride or hydrogen chloride, in contrast, gave somewhat greater value in R_F, where the halides seemed to move forming salts with picoline (see the foot-note marked with § in the table).

The butanol-propanol system proved also useful as a solvent, although differences among R_F values of the chloride, bromide, and iodide became somewhat smaller, whereas butanol-ammonia gave too small R_F values for all halides and only too small differences among them to distinguish spots clearly. Only in the case of iodide, which often appears as a partly diffused spot on a butanol-picoline chromatogram, development with either one of the other two solvents, if necessary, will be useful.

Influence of alkali on the chromatogram.—As the decomposition solution of organic halogenocompound is alkaline, the influence of alkali on the chromatogram was examined using 0.1 *M* solutions of halides in 0.5~3.0 *N* sodium hydroxide. As shown in the table, an aqueous caustic soda was found to decrease slightly the R_F values of halides with an increase in its concentration. It may, however, be considered that no such remarkable effect as to disturb identification of halides was seen in practice on the R_F values or on the shapes of the spots, so far the concentration of alkali lower than *ca.* 1.5 *N* was used.

Chromatograms of the decomposition solutions of organic substances containing halogens.—According to the directions given before for the decomposition of organic substances, just an alkaline solution of 1~1.5 *N* concentration should be prepared, in which practically no influence on the spots of halides could be observed as described above.

R_F values with butanol-picoline of halides of such solutions obtained from various organic halogenocompounds used alone or in some admixtures, either containing nitrogen and sulfur in addition to halogen or not, were always in good agreement respectively with those obtained in control experiments (see the table), shapes of the spots being also unaffeted. Halogen of organic compound containing one atom at least per molecular weight 1,000 is to be successfully identified by this procedure, taking into account the limit of detection observed before with control test.

When the solution to be tested, if necessary, is applied by the side of or mixed with an authentic specimen of sodium halide in question and developed, the resulting figure will add a more reliable fact. Separation and identification of halogens in organic compounds were thus found satisfactory.

The present method of analysis seems to be applied also to the solution obtained microtechnically by decomposing organic halogenocompound on heating with the mixture of magnesium and anhydrous potassium carbonate (Foulke-Schneider method[4]). But no solvent could yet be found applicable for the solution obtained by the Carius method of decomposition with fuming nitric acid.

Chromatograms of sulfide and rhodanate.—In the case of an organic substance containing nitrogen or sulfur, or both together, there may be produced cyanide or sulfide, or both and sometimes rhodanate in the decomposition solution with sodium. Accordingly, specimens of such salts were also developed.

When revealed in the usual way except washing with water instead of with dilute nitric acid, sodium cyanide showed only a very faint spot near the original point with every solvent used in the experiment. Sodium sulfide gave a spot of low R_F value as shown in the table merely by spraying with aqueous silver nitrate. By the usual method of revelation, on the contrary, potassium rhodanate alone or even in admixture with halides showed a spot located always above that of iodide in case of every solvent, as shown in the last column of the table. In fact, on dealing with the solution from an organic compound containing (besides halogens) both nitrogen and sulfur, such a spot often appeared just at the point accounted above.

It was thus confirmed that these salts gave influence neither upon R_F values nor on shapes of halides existed together.

Summary

Paper chromatograms of sodium halides such

(3) It appears that each halide moves mainly in a form of the salt as it was. When developed with butanol-picoline, especially when halides dissolved in water were used, a faint ghost was always found just above each spot of halides, and seemed likely to consist of a salt of picoline with halide ion partly separated.

(4) G. Foulke and F. Schneider, *Ind. Eng. Chem., Anal. Ed.*, **10**, 102 (1938).

as chloride, bromide, and iodide, dissolved in water or in aqueous caustic soda of various concentrations, were studied with butanol-picoline, butanol-propanol, or butanol-ammonia as a developing solvent, in order to identify such halides accurately by their R_F values on chromatograms, and further to apply the result for the identification of halogens contained in organic substances.

The spots of halides after development were revealed by their brown coloration of silver sulfide formed through silver halides. Iodide was better identified by means of a characteristic starch method.

It was found that butanol-picoline was a suitable solvent to separate spots of the three halides completely, and that these suffered little influence on R_F value or on shape by caustic soda contained in solutions so far as its concentration was within *ca.* 1.5 *N*. Sodium cyanide and sulfide, and potassium rhodanate were also chromatographed and it was found that they were located quite separately from halides and did not disturb the identification of the latter.

On chromatographing a few drops of the decomposition solution with sodium (the alkaline concentration being within the limit quoted above) of various organic substances, which, in addition to halogen, may sometimes contain either nitrogen or sulfur, or both together, halogens contained in them were identified quite satisfactorily based on the results obtained above.

The authors wish to express their hearty thanks to the Ministry of Education for the Scientific Research Grant given for this work.

Institute of Science and Technology,
Tokyo University, Komaba-machi,
Meguro-ku, Tokyo

Estrogenic Action and Molecular Structure

By Michinori ŌKI and Yoshiyuki URUSHIBARA

(Received November 20, 1951)

This paper presents a hypothesis regarding an optimum molecular thickness as a structural requirement for the development of a strong estrogenic activity.

The preparation of various estrogenic oxygen and sulfur analogs of hexestrol or its dimethyl ether, reported from this laboratory,[1),2),3)] has demonstrated that the similarity in the structural features, consisting of the shapes of molecular skeletons and the nature and the positions of functional groups, may cause similar physiological properties. It was shown by X-ray crystallography[4)] that the stereochemical arrangement of the atoms in hexestrol is very closely related to the stereochemical form of the natural estrogens. On the other hand, diethylstilbestrol would possess a planar structure, significantly thinner than those of hexestrol and natural estrogens, if its two ethyl groups did not exert a steric interference upon the benzene nuclei and thus the whole system were completely conjugated.

F. W. Schueler[5)] suggested that a given substance may be estrogenic if it consists of a rather large, rigid, and inert molecular structure with two active hydrogen bond-forming groups located at an optimum distance of 8.55 A. from one another. E. R. Clark[6)] modified Schueler's hypothesis by introducing the conception of "anchoring" in order to explain the estrogenic activity of non-rigid molecules. There are, however, many substances which have little activity even though they apparently satisfy Schueler's requirements, as exemplified by 4, 4'-dihydroxystilbene and 4, 4'-dihydroxy-2, 2'-diethylstilbene. Schueler seems to find an example to meet his hypothesis in *trans-p, p'*-dihydroxyazobenzene which is said to show definite estrogenic activity in dosages of from 10 to 15 mg. when injected subcutaneously in

(1) Yoshiyuki Urushibara and Michinori Oki, this Bulletin, **23**, 35 (1950).
(2) Y. Urushibara and Takeyoshi Takahashi, *ibid.*, **23**, 53 (1950).
(3) Y. Urushibara, M. Oki, and Reiji Ikeda, *ibid.*, **25**, 66 (1952).
(4) C. H. Carlisle and D. Crowfoot, *J. Chem. Soc.*, **1941**, 6.
(5) F. W. Schueler, *Science*, **103**, 221 (1946).
(6) E. R. Clark, *J. Chem. Soc.*, **1950**, 3397.

rats. But it should be considered that this substance is rather weak in spite of its fulfilment of the requirements, because Schueler gives examples of substances more active but not meeting his requirements.

The present authors measured the absorption spectra and the extinction coefficients of 4,4'-dimethoxystilbene, $CH_3OC_6H_4CH=CHC_6H_4OCH_3$, and its α,α'-dialkyl homologs. They are shown in the accompanying figure with the absorption curve of *p*-cresol methyl ether. The unsubstituted dimethoxystilbene shows a maximum at the longest wave length with the greatest molecular extinction coefficient. The dimethyl homolog gives a maximum at a shorter wave length and a smaller molecular extinction coefficient, and, as a larger alkyl group is substituted, the absorption curve is displaced further toward a shorter wave length and a smaller molecular extinction coefficient, until, presumably, that of *p*-cresol methyl ether is reached at the extremity.

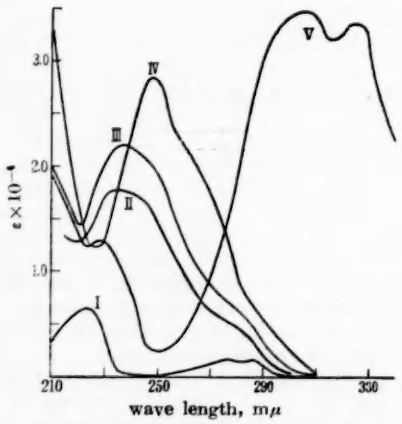


Fig. 1.—Ultraviolet absorption spectra of *p*-cresol methyl ether (I), 4,4'-dimethoxy-α,α'-dipropylstilbene (II), 4,4'-dimethoxy-α,α'-diethylstilbene (diethylstilbestrol dimethyl ether)(III), 4,4'-dimethoxy-α,α'-dimethylstilbene (IV), and 4,4'-dimethoxystilbene (V) in 95% ethanol.

The displacement of the absorption curves from that of unsubstituted dimethoxystilbene can be interpreted as showing the extent of decrease in the degree of conjugation, which in turn can be attributed to a deviation of the benzene nuclei from the coplanar structure due to a rotation about the 1,4- and 1',4'-axes enforced by the steric interference of the alkyl groups at the α,α'-positions. Then, it will be proved that diethylstilbestrol does not possess a planar structure, and it is natural to suppose that it will possess an optimum molecular thickness (the dimension perpendicular to the plane of the ordinary projection formula) as the most potent member of its series. Since steric interference is mutual, the two ethyl groups may not be able to rotate freely or independently of the benzene nuclei. Thus, the ethyl groups will be arranged in a manner coördinated with the rotated benzene nuclei, and it can be said that the ethyl groups impart the most appropriate structural features to the molecule of diethylstilbestrol by their own bulks on one hand, and, on the other, by exerting a steric interference on the benzene nuclei to cause their deviation from a coplanar conjugation.

It must be noticed that the molecular thickness is of course correlated with the width for a given structural formula and the width may possibly have no less importance on the physiological properties, but the thickness is mentioned here to express explicitly the significance of the definite deviation from a planar structure and to put a primary stress on the nature of the flatness of the molecule, because the natural estrogens and consequently hexestrol are known to possess rather flat structures.

Examination of scale models also reveals that diethylstilbestrol is sterically hindered while the 2,2'-diethyl isomeride is not hindered. There exists no steric interference in 4,4'-dihydroxystilbene as is shown by the absorption spectrum of its dimethyl ether and also in *trans*-*p*,*p*'-dihydroxyazobenzene as is understood from its constitution. The small activity of these substances capable of taking the most conjugated planar structures can be explained by considering that their structures are too thin to develop a strong activity although they are favored with the location of the two hydrogen bond-forming groups at the optimum distance.

In a previous paper[3] the authors and R. Ikeda described the synthesis of 1,2-bis-(*p*-methoxyphenyl)-1,2-bis-(methylthio)-ethylene, $CH_3OC_6H_4C(SCH_3)=C(SCH_3)C_6H_4OCH_3$, which was active in the dosage of 10γ in mice. It gave an absorption spectrum indicating that the steric interference of the methylthio groups corresponds nearly to that of the propyl groups in 4,4'-dimethoxy-α,α'-dipropylstilbene.

In this connection, it may be pointed out that it is dangerous to attempt a determination of *cis*- and *trans*-forms of stilbene derivatives from absorption spectra.[7]

(7) D. H. Hey and O. C. Musgrave, *J. Chem. Soc.*, **1949**, 3156.

Experimental Part

The absorption spectra were recorded with a Beckman Model DU photoelectric quarz spectrophotometer. The length of solutions was 5 mm. The concentrations of the solutions are shown below: *p*-Cresol methyl ether (b. p. 176°) 17.75×10^{-5} mol./l.
4,4'-Dimethoxystilbene (m. p. 212—213°) 5.25 〃
4,4'-Dimethoxy-α,α'-dimethylstilbene (m. p. 140.5—142°) 5.26 〃
4,4'-Dimethoxy-α,α'-diethylstilbene (Diethylstilbestrol dimethyl ether) (m. p. 121.5—123°) 2.80 〃
4,4'-Dimethoxy-α,α'-dipropylstilbene (m. p. 111—113°) 6.45 〃

4,4'-Dimethoxystilbene, $CH_3OC_6H_4CH=CHC_6H_4OCH_3$. Prepared by the methylation of 4,4'-dihydroxystilbene.

4,4'-Dimethoxy-α,α'-diethylstilbene (Diethylstilbestrol dimethyl ether), $CH_3OC_6H_4C(C_2H_5)=C(C_2H_5)C_6H_4OCH_3$. Synthesized by the method of Vargha and Kovács.[8]

***p*-Methoxyacetophenone-hydrazone,** $CH_3OC_6H_4C(CH_3)=NNH_2$. *p*-Methoxyacetophenone (5.0 g.), prepared from anisole and acetic anhydride,[9] and 72% hydrazine hydrate (3.3 g.) were dissolved in warm alcohol (5 cc.) and the solution was heated on a water bath for 5 hours. After cooling, the formed crystalline product was collected and recrystallized from alcohol. Colorless needles (Yield 5.0 g.), m. p. 118.5—120°. Found: N, 17.03%. Calculated for $C_9H_{12}ON_2$: N, 17.06%.

4,4'-Dimethoxy-α,α'-dimethylstilbene, $CH_3OC_6H_4C(CH_3)=C(CH_3)C_6H_4OCH_3$. The above hydrazone (4.0 g.) and yellow mercuric oxide (8.0 g.) suspended in petroleum ether (b. p. 40—60°) (100 cc.) were shaken at 23—24° for 16 hours. The resulting red solution was filtered and sulfur dioxide was passed vigorously into the solution under cooling, until the color disappeared and instantly bubbles were generated. Petroleum ether was evaporated and the residue was heated to 150° to complete decomposition. The substance, dissolved in benzene, was adsorbed chromatographically on alumina and recrystallized from alcohol. Colorless plates (Yield 0.6 g.), m. p. 140.5—142°. Found: C, 80.45; H, 7.59%. Calculated for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Dodds *et al.*[10] give m. p. 127—128°.

4,4'-Dimethoxy-α,α'-dipropylstilbene, $CH_3OC_6H_4C(C_3H_7)=C(C_3H_7)C_6H_4OCH_3$. *p*-Methoxybutyrophenone, prepared from anisole and butyryl chloride,[11] gave a difficultly crystallizable hydrazone. The crude hydrazone (5 g.) and yellow mercuric oxide (10 g.) were treated in the same way as described above. Recrystallized from alcohol, the product was obtained in colorless rhombic prisms (Yield 0.3 g.), m. p. 111—113°. Found: C, 81.77; H, 8.90%. Calculated for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70%. The minimum active dose in mice was found 100 γ. Dodds *et al.*[10] give a boiling point 178—181°/0.8 mm. but no melting point. They record a minimum active dose of 100 γ in rats for the corresponding free phenol.

The authors thank the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

(8) F. L. Vargha and E. Kovács, *Ber.*, **75**, 794 (1942).
(9) J. B. Conant and C. R. Kinnet, "Org. Syntheses" Coll. Vol., I, p. 105.
(10) E. C. Dodds, L. Golberg, W. Lawson, and R. Robinson, *Proc. Roy. Soc.*, B, **127**, 140 (1939).
(11) P. M. Baranger, *Bull. soc. chim. France*, [4], **49**, 1214 (1931).

Estrogenic Thio-Analogs of the Dimethyl Ethers of Diethylstilbestrol, its Homologs, and Hexestrol

By Michinori ŌKI

(Received December 10, 1951)

The author and Y. Urushibara[1] have presented a hypothesis postulating that it is essential for a highly estrogenic substance to possess not only two groups carrying active hydrogen atoms, located at the optimum distance from one another,[2] but also a moderate thickness of the molecule. Estradiol is endowed *a priori* with such favorable structural features and hexestrol shares the fame of strong estrogens with the natural hormone due to its privilege of being a meso form, while diethylstilbestrol, which otherwise would have a planar structure, acquires its molecular thickness qualifying it for an estrogen of the same rank through the steric interference between the benzene rings and the ethyl groups, the former enforced to rotate to a moderate extent and the latter arranged in a coördinated manner. The steric interference and the rotation of the benzene rings caused by it have been deduced from a comparison of the absorption spectra of the dimethyl ethers of diethylstilbestrol and its lower and higher homologs with that of the unsubstituted 4, 4′-dimethoxystilbene on the assumption that the deterioration in the light absorption is associated with the loss in conjugation.

The substitution of the methoxy group or the methylthio group for the ethyl groups in hexestrol and diethylstilbestrol may cause no radical change in the shapes of the molecules. Thus, various oxygen and sulfur analogs in this line have been synthesized and proved to be estrogenic as reported from this laboratory.[3],[4],[5]

The present paper contains the following thio-analogs, derived from dimethyl ethers of diethylstilbestrol, its homologs, and hexestrol, by replacing the phenolic oxygen atoms with sulfur atoms. The methods of preparation of these substances are described in the Experimental Part.

4, 4′-Bis-(methylthio)-α, α'-dimethylstilbene, $CH_3SC_6H_4C(CH_3)=C(CH_3)C_6H_4SCH_3$ (I)

4, 4′-Bis-(methylthio)-α, α'-diethylstilbene, $CH_3SC_6H_4C(C_2H_5)=C(C_2H_5)C_6H_4SCH_3$ (II)

4, 4′-Bis-(methylthio)-α, α'-dipropylstilbene, $CH_3SC_6H_4C(C_3H_7)=C(C_3H_7)C_6H_4SCH_3$ (III)

4-Methoxy-4′-(methylthio)-α, α'-diethylstilbene, $CH_3OC_6H_4C(C_2H_5)=C(C_2H_5)C_6H_4SCH_3$ (IV)

3, 4-Bis-[*p*-(methylthio)-phenyl]-hexane, $CH_3SC_6H_4CH(C_2H_5)CH(C_2H_5)C_6H_4SCH_3$ (V)

The steric arrangements of the groups constituting the molecular skeletons of these compounds are expected to be similar to those of the corresponding dimethoxy compounds, because the skeletons of the members of the present series are constructed in the same manner as those of the corresponding members of the dimethoxy series. The absorption data of the unsaturated members presented in Table 1 show that the steric interference and consequently the rotation of the benzene rings caused by it grow greater as the alkyl groups at the α, α'-positions become larger (I, II and III), although the maxima are displaced in the whole to longer wave lengths than in the dimethoxy series probably due to the influence of the methylthio groups. It is noticed that the absorption spectrum of substance IV, a combination of one half each of the corresponding dimethoxy and dimethylthio compounds, shows two maxima, one being located very close to the maximum (236 mμ) of the dimethoxy compound, namely, diethylstilbestrol dimethyl ether, and the other to that of the

Table 1

Substance	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.} \times 10^{-4}$
I	271	3.1
II	266.5	2.7
III	265	2.5
IV	233	1.2
	263.5	2.0

(1) M. Ōki and Y. Urushibara, this Bulletin, **25**, 109 (1952).
(2) F. W. Schueler, *Science*, **103**, 221 (1946).
(3) Y. Urushibara and M. Ōki, this Bulletin, **23**, 35 (1950).
(4) Y. Urushibara and T. Takahashi, *ibid.*, **23**, 53 (1950).
(5) Y. Urushibara, M. Oki, and R. Ikeda, *ibid.*, **25**, 66 (1952).

dimethylthio compound (II).

It is expected that the methylthio group, as well as the methoxy group, is demethylated *in vivo*, and thus two hydrogen bond-forming groups required for the development of estrogenic activity become available in these substances, although the distance between them may be a little greater than in the corresponding dihydroxy compounds, and the thiol group to be formed by demethylation may be subject to ready oxidation to a disulfide group *in vivo*. Estrogenic activities were evaluated by the vagina smear test with ovariectomized mice by subcutaneous injection of oil solutions in two portions. Substance I produced estrus in 50% of animals in the dosage of 300 γ. Substance II was fully active in 40 γ. Substance III showed activity, partially incomplete, in all the animals used in the dosage of 200 γ. Here, too, in the dimethylthio series, the medium member with a moderate molecular thickness shows the greatest activity. Substance IV was found very potent, being fully active in all the animals used in the dosage of 5 γ, while diethylstilbestrol dimethyl ether showed a minimum active dose of 2.5 γ by the same test method. Substance V showed an unexpectedly small potency, its minimum active dose being 200 γ. It may possibly be a racemic form instead of a meso form, which is also made probable by its low melting point and high solubility in organic solvents.

Experimental Part

The preparation of 4,4′-Bis-(methylthio)-α,α′-dialkylstilbenes

***p*-(Methylthio)-acetophenone**, $CH_3SC_6H_4COCH_3$. To a mixture of 12.4 g. of thioanisole, prepared from thiophenol and dimethyl sulfate[6] and dissolved in 30 cc. of carbon disulfide, and 20.0 g. of aluminum chloride, 7.9 g. of acetyl chloride was gradually added with thorough cooling and stirring. The mixture was left to stand for 2 hours and then gently boiled for 30 minutes. After being treated with ice and hydrochloric acid (30 cc.), the mixture was extracted with benzene. The benzene solution was washed with 10% aqueous sodium hydroxide and with water, dried over calcium chloride, and distilled. *p*-(Methylthio)-acetophenone distilled over at 154-156°/12 mm. and was recrystallized from petroleum ether. Colorless prisms, m. p. 84°. Yield 10.5 g. (63% of the theory). Found: S, 19.36%. Calculated for $C_9H_{10}OS$: S, 19.29%.

The structure of the ketone was proved by its oxidation to *p*-methanesulfonylbenzoic acid, $CH_3SO_2C_6H_4CO_2H$. Namely, oxidation with potassium bichromate and 50% sulfuric acid gave a substance melting at 268-268.5° and containing S, 16.05%. *p*-Methanesulfonylbenzoic acid melts at 267-268°[7] and requires S, 16.02%.

***p*-(Methylthio)-acetophenone-hydrazone.** A Mixture of 3.5 g. of *p*-(methylthio)-acetophenone dissolved in 5 cc. of hot alcohol and 2.7 g. of 72% hydrazine hydrate was refluxed for 5 hours. The crystalline product was recrystallized from benzene-petroleum ether. *p*-(Methylthio)-acetophenone-hydrazone was obtained in colorless leaflets melting at 96-96.5°. Yield 3.7 g. (97% of the theory). Found: N, 15.53; S, 17.55%. Calculated for $C_9H_{12}N_2S$: N, 15.54; S, 17.79%.

4,4′-Bis-(methylthio)-α,α′-dimethylstilbene (I). A suspension of 4.0 g. of *p*-(methylthio)-acetophene-hydrazone and 9.0 g. of yellow mercuric oxide in 100 cc. of petrolem ether was shaken for 8 hours at 22-23°. The resulting red solution was filtered from solids and sulfur dioxide was rapidly introduced, when yellowish crystals separated out. The solvent was distilled off, the remainder was dissolved in benzene, and the benzene solution was passed through an aluminum oxide column. From the colorless part of the column, 4,4′-(methylthio)-α,α′-dimethylstilbene was obtained in colorless needles melting at 132.5-133.5° after recrystallization from alcohol. Yield 0.3 g. Found: S, 21.39%. Calculated for $C_{18}H_{20}S_2$: S, 21.35%.

***p*-(Methylthio)-propiophenone**, $CH_3SC_6H_4CO-C_2H_5$. Prepared in the same way as *p*-(methylthio)-acetophenone, using 9.3 g. of propionyl chloride instead of 7.9 g. of acetyl chloride. *p*-(Methylthio)-propiophenone distilled at 167-169°/14 mm. Recrystallized from petroleum ether, it was obtained in colorless prisms melting at 59-60°. Yield 12.2 g. (68% of the theory). Found: S, 17.95%. Calculated for $C_{10}H_{12}OS$: S, 17.79%. The structure was proved by its transformation into *p*-methanesulfonylbenzoic acid.

***p*-(Methylthio)-propiophenone-hydrazone.** Prepared from 3.0 g. of *p*-(methylthio)-propiophenone and 1.0 g. of hydrazine hydrate, and recrystallized from benzene-alcohol. Colorless prisms, m. p. 75.5-76.5°. Yield 3.0 g. (94% of the theory). Found: N, 14.52; S, 16.73%. Calculated for $C_{10}H_{14}N_2S$: N, 14.42; S, 16.50%.

4,4′-Bis-(methylthio)-α,α′-diethylstilbene (II). A suspension of 4.0 g. of *p*-(methylthio)-propiophenone-hydrazone and 8.0 g. of yellow mercuric oxide in 50 cc. of petroleum ether was shaken for 6 hours at 16-18°, and the reaction mixture was treated in a manner similar to the case of 4,4′-bis-(methylthio)-α,α′-dimethylstilbene. A chromatographical separation followed by recrystallization from alcohol gave 4,4′-bis-(methylthio)-α,α′-diethylstilbene in colorless rhombic prisms melting at 132-132.5°. Yield 0.5 g. Found: S, 19.83%. Calculated for $C_{20}H_{24}S_2$: S, 19.52%. The same substance was obtained by catalytic hydrogenation of the reaction products with colloidal

(6) H. Gilman and N. J. Beaber, *J. Am. Chem. Soc.*, **47**, 1449 (1925).

(7) J. Walker, *J. Chem. Soc.*, **1945**, 630.

palladium in acetic acid followed by recrystallization from ethyl acetate.

A direct recrystallization of the products from alcohol gave *p*-(methylthio)-propiophenone-azine, m. p. 139-140°, identified with the specimen described below, and a small yield (0.01 g.) of a compound in prisms melting at 70-73° from the mother liquor. The latter is presumably *cis*-4, 4'-bis-(methylthio)-α, α'-diethylstilbene. Found: S, 19.30%. Calculated for $C_{20}H_{24}S_2$: S, 19.52%.

p-(Methylthio)-butyrophenone, $CH_3SC_6H_4CO\text{-}C_3H_7$. Prepared in the same way as *p*-(methylthio)-acetophenone, 10.7 g. of butyryl chloride being used. *p*-(Methylthio)-butyrophenone distilled at 168.5-171.5°/13 mm. Recrystallization from petroleum ether gave colorless needles melting at 69.5-70.5°. Yield 11.7 g. (61% of the theory). Found: S, 16.80%. Calculated for $C_{11}H_{14}OS$: S, 16.50%. The structure was proved by the formation of *p*-methanesulfonylbenzoic acid on oxidation.

p-(Methylthio)-butyrophenone-hydrazone. Prepared analogously from 9.5 g. of the above ketone and 4.5 g. of 72% hydrazine hydrate in 10 cc. of alcohol. Colorless needles, m. p. 71-72°. Yield 9.0 g. (90% of the theory). Found; N, 13.31; S, 15.35%. Calculated for $C_{11}H_{16}N_2S$: N, 13.45; S, 15.39%.

4, 4'-Bis-(methylthio)-α, α'-dipropylstilbene (III). Synthesized analogously to its lower homologs. Chromatographical separation with alumina and recrystallization from alcohol gave colorless prisms melting at 99-99.5°. Yield 0.2 g. from 4.0 g. of the hydrazone. Found: S, 18.22%. Calculated for $C_{22}H_{28}S_2$: S, 17.99%.

From the mother liquor of recrystallization a small amount of a viscous oil, presumably the *cis*-isomeride, was obtained, but not characterized.

The Preparation of 4-Methoxy-4'-(methylthio)-α, α'-diethylstilbene (IV)

The steps of synthesis are shown below schematically:

$$p\text{-}NO_2C_6H_4CH_2COCl + C_6H_5SCH_3 \rightarrow p\text{-}NO_2C_6H_4CH_2COC_6H_4SCH_3\text{-}p$$

$$\rightarrow p\text{-}NO_2C_6H_4CH(C_2H_5)COC_6H_4SCH_3\text{-}p$$

$$\rightarrow p\text{-}H_2NC_6H_4CH(C_2H_5)COC_6H_4SCH_3\text{-}p$$

$$\rightarrow p\text{-}HOC_6H_4CH(C_2H_5)COC_6H_4SCH_3\text{-}p \quad \text{(not isolated)}$$

$$\rightarrow p\text{-}CH_3OC_6H_4CH(C_2H_5)COC_6H_4SCH_3\text{-}p$$

$$\rightarrow p\text{-}CH_3OC_6H_4CH(C_2H_5)\text{-}C(C_2H_5)(OH)C_6H_4SCH_3\text{-}p$$

$$\rightarrow p\text{-}CH_3OC_6H_4C(C_2H_5)=C(C_2H_5)C_6H_4SCH_3\text{-}p$$

p-Nitrobenzyl-p-(methylthio)-phenyl-ketone, $NO_2C_6H_4CH_2COC_6H_4SCH_3$. To a solution of 6.2 g. of thioanisole in 50 cc. of carbon disulfide 15.0 g. of aluminum chloride was added. *p*-Nitrophenylacetyl chloride, prepared from 10.0 g. of *p*-nitrophenylacetic acid and 11.6 g. of phosphorus pentachloride,[8] was dropped into the mixture while the solvent was gently boiled. The mixture was boiled further 30 minutes to complete the reaction. The upper carbon disulfide layer was decanted off and the greenish-black viscous addition compound was decomposed with ice and hydrochloric acid (30 cc.). The yellowish fine granular product was collected, and washed well with water. (Sodium hydroxide cannot be used to remove aluminum compounds because the ketone is soluble in caustic alkali in purple color.) Recrystallization from acetone gave pale yellow crystals melting at 183-185°. Yield 12.2 g. (85% of the theory). Found: N, 4.73; S, 11.40%. Calculated for $C_{15}H_{13}O_3NS$: N, 4.88; S, 11.16%.

1-(p-Nitrophenyl)-propyl-p-(methylthio)-phenyl-ketone, $NO_2C_6H_4CH(C_2H_5)COC_6H_4SCH_3$. The above ketone (25 g.) was added in small portions to a hot solution of 1.2 g. of metallic sodium in 50 cc. of absolute alcohol, when an intensive violet color resulted. The mixture was heated on a water bath for 15 minutes, cooled slightly, mixed with 8.0 g. of ethyl iodide, and heated again for 2 hours. When the violet color almost disappeared, an alcoholic solution containing 0.6 g. of sodium ethoxide and then 2.0 g. of ethyl iodide were added. The mixture was further refluxed until the violet color completely disappeared (about 2 hours). The resulting light-brownish solution with crystals of sodium iodide in it was poured into 100 cc. of water. Alcohol was evaporated off under a reduced pressure and the remainder was extracted with ether. The ethereal solution was washed with aqueous sodium thiosulfate and then with water, and evaporated. The residue was distilled under a reduced pressure. A viscous orange oil distilled at 202-205°/0.02 mm. Yield 11.0 g. (70% of the theory). On standing for a long time it solidified and was recrystallized from alcohol. Pale yellow needles, m. p. 64-65°. Found: N, 4.63; S, 10.06%. Calculated for $C_{17}H_{17}O_3NS$: N, 4.44; S, 10.17%.

1-(p-Aminophenyl)-propyl-p-(methylthio)-phenyl-ketone, $H_2NC_6H_4CH(C_2H_5)COC_6H_4SCH_3$. To a solution of 15.8 g. of the above ketone in 100 cc. of hot alcohol, 22.5 g. of granulated tin was added and 65 cc. of concentrated hydrochloric acid was gradually added in small portions. The mixture was refluxed until no violet coloration occurred on addition of a small portion to alcoholic sodium hydroxide (about 1.5 hours). On pouring the reaction mixture into 100 cc. of water a complex product separated out in a viscous brown oil soluble with difficulty even in hot water. After evaporation of alcohol *in vacuo*, the oily addition product and the upper hydrochloric acid layer were poured together into an excess of hot aqueous 10% sodium hydroxide, and the whole was boiled for a while to complete the decomposition of the addition product. A yellow viscous oil separated out and solidified on cooling. Recrystallized from benzene-petroleum ether,

(8) E. Wedekind, *Ann.*, **378**, 289 (1911).

the amino compound was obtained in colorless prisms melting at 100.5-102.5°. Yield 12.5 g. (81% of the theory). Found: N, 4.86; S, 11.56%. Calculated for $C_{17}H_{19}ONS$: N, 4.91; S, 11.23%.

1-(*p*-Methoxyphenyl)-propyl-*p*-(methylthio)-phenyl-ketone, $CH_3OC_6H_4CH(C_2H_5)COC_6H_4SCH_3$. The above amino compound (7.1 g.) and 20 cc. of 30% sulfuric acid were refluxed to a clear solution (about 15 minutes), which was poured on 100 g. of ice with vigorous stirring. To the resulting pasty mass 1.8 g. of sodium nitrite dissolved in 5 cc. of water was gradually added. After standing for 30 minutes the excessive nitrous acid was decomposed with urea. The diazonium sulfate solution was poured into 100 cc. of boiling 30% sulfuric acid in small portions while the mixture was kept boiling, and the whole was further boiled for a few minutes. A black viscous oil separated out, turning to a resinous mass on cooling. The aqueous layer was decanted off and the remainder was well washed with cold water. The phenol thus obtained could not be purified. The crude substance was dissolved in 25 cc. of 10% aqueous sodium hydroxide. (When 15% sodium hydroxide was used the sodium salt of the phenol could be dissolved in it with difficulty.) To the solution 4.0 g. of dimethyl sulfate was added with occasional shaking. The mixture was heated for 30 minutes on a water bath, then cooled, and extracted with benzene. The benzene extracts were dried over calcium chloride and evaporated. The methoxy compound distilled at 200-205°/0.15 mm. and solidified on cooling. Recrystallization from alcohol gave colorless needles melting at 76.5-78°. Yield 3.3 g. (44% of the theory). Found: S, 10.31%. Calculated for $C_{18}H_{20}O_2S$: S, 10.67%.

1-(*p*-Methoxyphenyl)-propyl-*p*-(methylthio)-phenyl-ethyl-carbinol, $CH_3OC_6H_4CH(C_2H_5)$-$C(C_2H_5)(OH)C_6H_4SCH_3$. A mixture of 3.0 g. of the above ketone dissolved in 10 cc. of warm benzene and a Grignard reagent prepared from 7.8 g. of ethyl iodide, 1.2 g. of magnesium, and 20 cc. of ether, was refluxed for 2 hours. Then the reaction mixture was treated with 50 cc. of 20% aqueous ammonium chloride and 50 g. of ice. The aqueous layer was extracted with benzene, and the combined benzene solution was dried over anhydrous sodium sulfate and evaporated. The residue gave a pale yellow oil distilling at 172-175°/0.14 mm. and boiling at 160-162°/0.10 mm. on redistillation. On standing, the distillate partially solidified and it was pressed on a porous plate. Recrystallization from alcohol gave colorless prisms melting at 75.5-77.5°. Yield 1.5 g. (45% of the theory). Found: S, 9.82%. Calculated for $C_{20}H_{26}O_2S$: S, 9.70%. The oily fraction contained perhaps a stereoisomeride with a lower melting point.

4-Methoxy-4'-(methylthio)-α, α'-diethylstilbene (IV). The above carbinol did not react with acetyl chloride and acetic anhydride.

The carbinol (0.5 g.) was fused with potassium bisulfate at 230-240° for 30 minutes. After cooling, the salt was washed out. On standing, the oily product partially solidified and was pressed on a porous plate. Recrystallization from alcohol gave colorless prisms melting at 107-108°. Yield 0.02 g. (4% of the theory). Found: S, 10.17%. Calculated for $C_{20}H_{24}OS$: S, 10.26%.

The Preparation of 3, 4-Bis-[*p*-(methylthio)-phenyl]-hexane (V)

***p*-(Methylthio)-propiophenone-azine,** $CH_3SC_6H_4$-$C(C_2H_5)=NN=C(C_2H_5)C_6H_4SCH_3$. A mixture of 30 g. of *p*-(methylthio)-propiophenone dissolved in 30 cc. of hot alcohol, 4.5 g. of hydrazine hydrate, and 7 cc. of acetic acid, was heated on a water bath, when suddenly a vigorous reaction took place and orange-colored crystals separated out. After completion of the reaction by heating further for 10 minutes, the reaction mixture was cooled and the crystalline product was collected. On recrystallization from benzene-alcohol the azine was obtained in yellow needles melting at 139.5-140°. Yield almost quantitative. Found: N, 8.16; S, 17.94%. Calculated for $C_{20}H_{24}N_2S_2$: N, 7.86; S, 17.99%.

3, 4-Bis-[*p*-(methylthio)-phenyl]-hexane (V). The above azine (1.0 g.) was suspended in a mixture of 20 cc. of methanol and 3 cc. of acetic acid, 0.1 g. of palladium chloride was added, and the mixture was shaken with hydrogen. Every time when the absorption of hydrogen slowed down, the evolved nitrogen was swept out from the hydrogenating apparatus, until no more hydrogen was absorbed. The solution filtered from the catalyst was diluted with water, when a pale yellow oil separated out and solidified on standing. Recrystallization from alcohol gave colorless plates melting at 62-63°. Yield 0.8 g. Found: S, 19.54%. Calculated for $C_{20}H_{26}S_2$: S, 19.40%.

The hydrogenation of the azine gave directly the ultimate product, and neither tetrahydro- nor dihydro-azine was isolated. It seems that the dihydro-azine is unstable and decomposed immediately to yield the dibenzyl compound and nitrogen.[9]

Ultra-Violet Absorption Spectra

The absorption spectra were recorded with a Beckman Model DU photoelectric quartz spectrophotometer in 95% ethanol solutions. The length of the solutions was 5 mm. Concentrations are given below:

Substance	Concentration
I	2.40×10^{-5} mol/l.
II	2.47
III	2.02
IV	2.76

The author thanks Professor Y. Urushibara for his kind guidance and encouragement.

(9) Cf. H. Bretschneider, A. de Jongo-Bretschneider, and N. Ajtai, *Ber.*, **74**, 571 (1941); Z. Földi and G. von Fodor, *ibid.*, **74**, 589 (1941); B. R. Baker, *J. Am. Chem. Soc.*, **65**, 1574 (1943).

Thanks are due also to Mr. F. Ueno of the Teikoku Hormone Manufacturing Co., Ltd., Kawasaki, for the bio-assays and to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

The Photopolymerization of Acetylene. On the Formation of Cyclooctatetraene

By Zenichiro KURI and Shoji SHIDA

(Received October 1, 1951)

Introduction

Ultraviolet light of wave lengths shorter than 2537 Å. induces polymerization of gaseous acetylene. A considerable number of investigations have been made on this reaction, concerning the reaction rate[3],[7],[8] and the reaction mechanism[4],[5],[9],[10] as well as the reaction products.[1],[2],[4],[6],[10]

The photopolymerization of acetylene is generally assumed to be propagated by a chain mechanism. Polymer is formed by the successive addition of acetylene molecules to the activated ones. The dimer of the chain polymerization is considered to be vinylacetylene by W. Kemula and S. Mrazek,[4] while recently B. L. Dunicz[10],[11] assumes that the dimer consists of cyclobutadiene, which so far has not been found to exist. Dunicz makes this assumption from the following facts; the reaction of mixtures of acetylene and vinylacetylene proceeds in a different way from that of acetylene only, and the cyclobutadiene structure has the considerable stability in its triplet state according to the theory of Wheland.[12]

From the cyclobutadiene theory of Dunicz, assuming the following reaction,

$$2C_4H_4(\text{Cyclobutadiene}) \rightarrow C_8H_8(\text{Cyclooctatetraene})$$

we expected cyclooctatetraene to form in the process of the photochemical change of acetylene. We investigated it in detail.

Experiments and Results

(1) Photochemical Properties and Analysis of Cyclooctatetraene (abbr. C. O. T.)

Photochemical Change of C. O. T.—It is not known whether C. O. T. changes photochemically or not, under the ultraviolet light. We tested it and found that C. O. T. in the gaseous state made the photochemical change in the irradiation of ultraviolet light. Spectra of irradiated C. O. T. show two new absorption bands, one of which is characteristic for benzene and the other one is of unknown substances. But the irradiation of one minute or

Fig. 1.—Photolysis of C. O. T.: (1) spectrum at the pressure of 0.1 mm. Hg; (2) the same at the lower pressure. (Spectrum of benzene is seen.); (3) and (4) iron spectrum.

(1) D. Berthelot and H. Gaudechon, *Compt. rend.*, **150**, 1169 (1910).
(2) S. Kato, *Bull. Inst. Phys. Chem. Research (Tokyo)* **10**, 343 (1931).
(3) S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, **54**, 94 (1932).
(4) W. Kemula and S. Mrazek, *Z. Physik. Chem.*, **B23**, 358 (1933).
(5) S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, **56**, 1550 (1934).
(6) R. Livingston and C. H. Schiflett, *J. Phys. Chem.*, **38**, 377 (1934).
(7) J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, **3**, 338 (1935).
(8) H. W. Melville, *Trans. Faraday Soc.*, **32**, 258 (1936).
(9) W. Kemula and B. L. Dunicz, *Z. Phys. Chem.*, **181**, 389 (1938).
(10) B. L. Dunicz, *J. Am. Chem. Soc.*, **63**, 2461 (1941).
(11) B. L. Dunicz, *J. Chem. Phys.*, **12**, 37 (1944).
(12) G. W. Wheland, *Proc. Roy. Soc. (London)*, **A164**, 397 (1938).

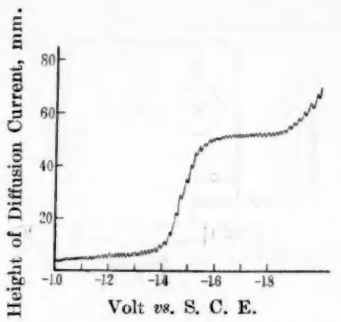


Fig. 2.—Polarogram of 4.6×10^{-4} M solution of C. O. T.: the diffusion current is 4.8 μA and the half wave potential is -1.49 volts *vs.* S. C. E. The sensitivity is 1.2×10^{-7} ampere per mm.

Fig. 3.—Spectra of the products: (5) photopolymerization products at 1.5 mm. Hg; (2) the same products at 0.5 mm. Hg; (1) (3) (4) and (6) iron spectra.

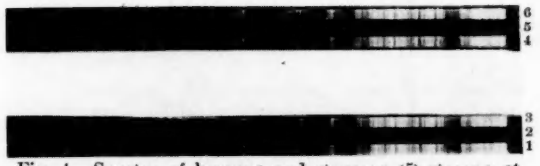


Fig. 4.—Spectra of benzene and styrene: (5) styrene at 0.2 mm. Hg; (2) benzene at 0.1 mm. Hg. (1) (3) (4) and (6) iron spectra.

two does not change the character of absorption spectra of C. O. T. So, in order to get C. O. T., acetylene should be passed in a few seconds under the ultraviolet light, avoiding the photolysis of C. O. T. It is to be found in Fig. 1.

Polarography of C. O. T.—The best way for the quantitative analysis of C. O. T. is the polarographic method.[13] We adopted Elofson's receipt as follows: Ethanol solution of C. O. T. 1 cc., 0.1 M solution of tetramethylammonium bromide 1 cc., sodium sulfite solution 0.1 cc.

The half wave potential was -1.49 volt *vs.* S. C. E. at pH=7. The diffusion current was linear against the concentration of C. O. T. from 1×10^{-5} to 2×10^{-3} M solution. At the sensitivity of 2.4×10^{-3} μA/mm. of the galvanometer, one mm. displacement of the diffusion current corresponds to 2.79×10^{15} molecules of C. O. T. in the cell solution mentioned above. Fig. 2 shows one of the polarograms of C. O. T.

(2) Irradiation of Acetylene in a Continuous Flow

(a) Products of the Reaction.—In order to obtain a larger fraction of the lower polymers, especially smaller than C_8H_8, formed during the reaction, products of irradiation were quickly removed out of the reaction tube to be frozen into the trap cooled by the dry ice at the end of the tube. After passing the dry ice trap, unchanged acetylene was frozen out into another trap cooled by the liquid air.

After the experiment, the thin yellow film was visible at the wall right in front of the light source mercury lamp and a light yellow volatile liquid stayed in the dry ice trap.

Fig. 3 gives the absorption spectra of the products at the pressures of 0.5 and 1.5 mm. Hg respectively. Spectra of pure benzene and pure styrene are given in Fig. 4. Besides benzene, we see a small amount of styrene in the spectral lines characterized by 2877, 2800, and 2780 Å. 2808, 2720, and 2687 Å. lines belong to the unknown substance which is called "c" group and is expected to correspond to acetylene-1-cyclobutene-1 by Dunicz.

C. O. T. was analysed by polarographic method dissolving the products in the cell solution of Elofson's receipt. We found a small but definite quantity of C. O. T., as was expected.

(b) The Rate of Formation of C. O. T. under the Varied Light Intensity.—Acetylene was made to flow continuously through the reaction tube irradiated with the mercury lamp at the space velocity of 2 cm./sec. and at the pressure of 175 mm. Hg for 180 minutes in each experiment. The total gas volume which flowed was 1.45×10^5 cc. and the passing time under mercury light was 5 sec. Light intensity of mercury lamp was varied by the electric current intensity from 3 to 10.4 amp. and was proportional to the current intensity. The weaker light intensity was obtained by the net screening.

The result is shown in Fig. 5. The amount of C. O. T. in 180 minutes, H, expressed in mm. of diffusion current of the polarograph at the sensitivity mentioned, is plotted against the abscissa i, the current intensity of mercury lamp. The maximum point was obtained at i=3.5 amp. Under the higher intensity of light, the amount of C. O. T. had decreased unexpectedly.

(13) R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

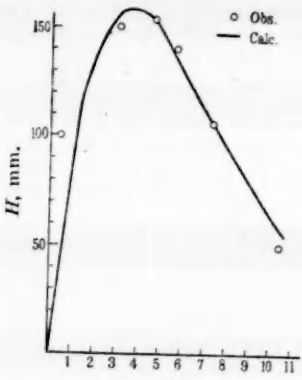


Fig. 5.—Rate of formation of C. O. T. *vs.* intensity of light.

A small percent of air added, quite obstructed the formation of C. O. T. perhaps by the oxydation. The use of a glass filter which is transparent 50% at 2600 Å., decreased the amount of C. O. T. but this was natural.

(c) The Rate of Formation of C. O. T. under the Varied Pressure of Acetylene. —Acetylene gas was made to flow in just the same way as in (2)-b, but the pressure was varied while the light intensity was maintained constant at 4.6 amp. Fig. 6 shows the results.

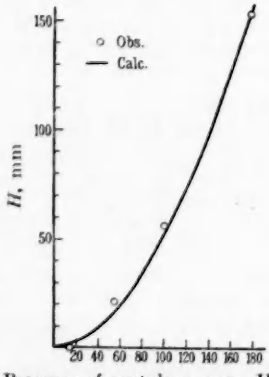


Fig. 6.—Rate of formation of C. O. T. *vs.* acetylene pressure.

The higher the pressure, the greater the rate of formation of C. O. T. However it is not linear to the pressure of acetylene but rather of somewhat higher exponents.

Experimental Details

Acetylene gas was purified by the normal method. The whole arrangement for the experiment is shown in Fig. 7. Purified acetylene is led through A into the liquid air freezing trap B, where the solidified acetylene is rid of the non-condensable gas through L and is fractionated into the reservoir C. From the reservoir, pure acetylene goes through a quartz reaction tube irradiated with mercury lamp E, passing the dry ice cooled trap F into the liquid air trap B. Pressure of acetylene in the tube is read by Bourdon gauge J or mercury manometer K. Reaction products caught in the trap F are evaporated into the reaction tube D, after evacuating the unchanged acetylene. The spectrographic system consists of a hydrogen lamp G, the reaction tube equipped with quartz windows on both ends, and a spectrograph H. An iron spark was used for the standard spectrum.

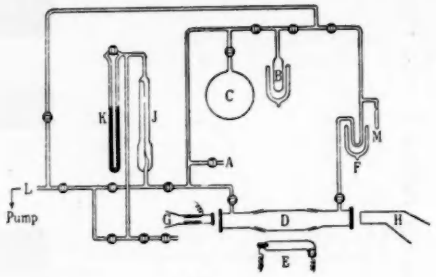


Fig. 7.

For the analysis of C. O. T., products in the trap F were directly distilled into a tiny ampoule M using the dry ice bath, and then the ampoule was cut at the top. Its contents were dissolved in ethanol-tetramethylammonium bromide solution which was submitted to polarographic analysis.

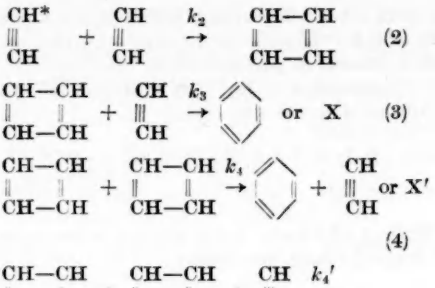
After each experiment, the reaction tube was heated in the air until the sediment on the wall had been removed.

Discussions of the Experimental Results

Now we have been able to find C. O. T. as one of the reaction products. Although straight chain dimers such as vinylacetylene can be an intermediate product, we can well expect on the basis of molecular structure that the steric factors for the formation of C. O. T. from such dimers are much smaller than that for the recombination of two cyclobutadiene molecules.

Assuming cyclobutadiene as dimeric intermediate, we propose the following reaction steps for the photopolymerization of acetylene, at least under the conditions employed.

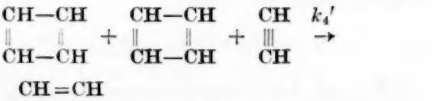
$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + h\nu \xrightarrow{k_1} \begin{matrix} CH^* \\ \| \\ CH \end{matrix} \qquad (1)$$

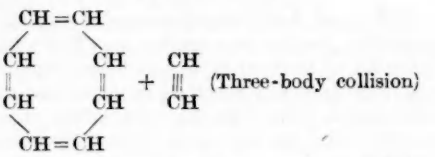


(2)

(3)

(4)





(4)′

For simplicity we will use the abbreviation: acetylene A; cyclobutadiene D; benzene B; C. O. T. C; trimers and tetramers of unknown structures X and X′ respectively. Under the condition of rapid flowing, we can ignore steps forming higher polymers than C_8H_8. Then in the stationary state

$$dA^*/dt = k_1 I_{abs} - k_2 A^* A = 0 \quad (5)$$

$$dD/dt = k_2 A^* A - k_3 DA - k_4 D^2 = 0 \quad (6)$$

$$dB/dt = k_3 DA \quad (7)$$

$$2dC/dt = k_4' D^2 A. \quad (8)$$

In Eq. (6) we ignored the consumption of D by (4′) compared with that by (3) and (4).

As cyclobutadiene formed is assumed to be in a higher energy (biradical or triplet) state, three-body collision would be necessary to couple one cyclobutadiene molecule with another to form C. O. T., which is a more stable form of C_8H_8. Bimolecular collision, on the contrary, will lead to the formation of either benzene and acetylene or some other substances. Benzene will be mainly formed by (3).

On the Light Intensity Absorbed.—Although we did not measure the absolute value of light intensity, the following considerations may be made on this respect. In Fig. 8, the light of intensity I_0 from the mercury lamp passes through the precipitated film on the wall of the reaction tube, where it diminishes to the intensity I. Then the light, being partially absorbed by acetylene, leaves the vessel with intensity I_t. Thus the light intensity absorbed by acetylene I'_{abs} is $I'_{abs} = I - I_t$. Here we assume that the time-

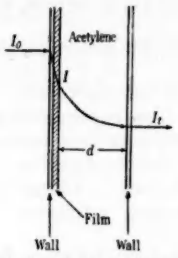


Fig. 8.—Mechanism of light absorption.

averaged light-absorbing power of the film produced in a definite time of irradiation is proportional to the light intensity I_0, *i. e.*, $I = I_0 e^{-I_0\beta}$, where β is a constant. On the other hand, the light intensity which passes through is represented by $I_t = Ie^{-\varepsilon Ad}$, where ε denotes the absorption coefficient of acetylene, A the concentration of acetylene, d the thickness of acetylene layer. So, $I'_{abs} = I - Ie^{-\varepsilon Ad} \fallingdotseq dI\varepsilon A$. Then the mean value of light absorbed per cm.^{3} across the layer is given by $I_{abs} = I'_{abs}/d = I\varepsilon A = I_0 \varepsilon A e^{-I_0\beta}$. The light intensity of the mercury lamp was found to be proportional to the current intensity i at constant voltage, *i. e.*, $I_0 = iq$, where q is a constant. Therefore

$$I_{abs} = \varepsilon A q i e^{-iq\beta} = QAie^{-i\alpha}, \quad (9)$$

where α and Q are constants.

Rate Equation of C. O. T. Formation.—From eqs. (5) and (6) we obtain as the stationary dimer concentration

$$D = [-k_3 A \pm (k_3^2 A^2 + 4k_1 k_4 I_{abs})^{1/2}]/2k_4. \quad (10)$$

Here the negative sign must be omitted. The rate constant k_4' is that for the three-body collision reaction and its collision factor is assumed to be 1/1000 of that for the binary collision of k_4 at the acetylene pressure A of 1 atm. Then

$$dC/dt = 1/2\, k'_4 D^2 A = 1/2000\, k_4 D^2 A, \quad (11)$$

where A is to be expressed in atm. unit and the same, zero or very small, activation energy is assumed for k'_4 and k_4. Inserting eq. (10) into eq. (11), we obtain

$$dC/dt = k_3^2/4k_4 \times 10^3 \cdot A^3[1 - \{1 + (2k_1 A/k_3^2 A^2/4k_4) I_{abs}\}^{1/2}] + k_1 A/2 \times 10^3 \cdot I_{abs}. \quad (12)$$

If the amount of C. O. T. produced is represented by H in terms of the height of

polarographic diffusion current, then

$$dC/dt = Hn/Vt \text{ molecules, cc.}^{-1} \text{ sec.,}^{-1}$$

where V is the total gas volume passed at the pressure under the experimental conditions, 1.45×10^5 cc., t the pass-time under irradiation, n sensitivity of polarograph for C. O. T. 2.79×10^{15} molecules mm.$^{-1}$ Using the values of constants given here, it follows

$$dC/dt = 3.84\times10^9 H = n_0 H. \quad (13)$$

From Eqs. (9), (12) and (13) we obtain finally

$$H = k_3^2 A^3/4k_4 n_0\times10^3[1-\{1+(2k_1Q/2n_0\times10^3 A^2/k^2{}_3A^3/4k_4n_0\times10^3)ie^{-i\alpha}\}^{1/2}] + k_1QA^2/2n_0\times10^3\cdot ie^{-i\alpha}. \quad (14)$$

Effect of Light Intensity.—The $H-i$ curve shown in Fig. 5 indicates the apparent effect of the light intensity on the rate of formation of C. O. T. Its true effect may be elucidated by using Eq. (14) as follows. At constant acetylene pressure A_0, putting

$$k^2{}_3A^3{}_0/4k_4n_0\times10^3 = a \quad (15)$$

and

$$k_1QA^2{}_0/2n_0\times10^3 = K, \quad (16)$$

we get

$$H = a[1-(1+2K/a\cdot ie^{-i\alpha})^{1/2}]+Kie^{-i\alpha}. \quad (17)$$

From $dH/di=0$, $i=1/\alpha$ or ∞ follows. Comparing this result with the experimental curve in Fig. 6, we obtain $\alpha=1/3.5$. When this value of α is inserted into Eqs. (15) and (16), the constants a and K can be determined from two equations with different values of i; that is, $a=4$ and $K=151$. As seen in the figure, the theoretical curve obtained from Eq. (17) using these values of a and K is in good agreement with the observed values.

If the steric factors, the collision numbers and the activation energy for the reactions (3) and (4) are denoted by P, Z and E respectively, Eq. (15) can be rewritten in the form

$$a = k^2{}_3A^3{}_0/4k_4n_0\times10^3 = P^2{}_3Z^2{}_3e^{-2E_3/RT}/4P_4Z_4e^{-E_4/RT}n_0\times10^3\cdot A^3{}_0. \quad (18)$$

Assuming[14] that $P_3=P_4=10^{-2}$ and that E_4 for the activation energy of the reaction between the two biradical (triplet) molecules is equal to zero, and using the values $n_0=3.84\times10^9$ molecules cc.$^{-1}$ sec^{-1}. mm.$^{-1}$, $A_0=175/760$ atm., $Z_3=Z_4=8.6\times10^{28}$ and $T=303$°K., we obtain $E=7.8$ Kcal./mol, which is not unreasonable for the activation energy of a propagation process in polymerization reaction.

Combination of Eq. (10) with Eqs. (15) and (16) leads to the expression

$$D = -k_3A/2k_4+k_3A/2k_4\cdot(1+2K/a\cdot ie^{-i\alpha})^{1/2}. \quad (19)$$

When $i=4.6$ amp., using the numerical values obtained above, we obtain

$$D = 1.85\times10^{-3} \text{ mm. Hg.}$$

Effect of Acetylene Pressure.—When the acetylene pressure was varied, even if the light intensity of mercury lamp remaining constant, the light intensity absorbed by acetylene was also varied. The light absorbing power of the colored film on the wall might therefore, possibly be changed with the pressure. However, this effect seemed to be relatively small and neglected, because the coloring of the film was observed to depend on the irradiating, not absorbed, intensity of light. Then, if we gather the constants in Eq. (14) as follows,

$$k^2{}_3/4k_4n_0\times10^3 = m \text{ and } k_1Q/2n_0\times10^3 = n,$$

Eq. (9) becomes

$$H = mA^3[1-(1+2n/mA\cdot ie^{-i\alpha})^{1/2}]+nA^2ie^{-i\alpha}. \quad (20)$$

The numerical values of m and n in the present experimental conditions are

$$m = a/A^3{}_0 = 3.28\times10^2 \text{ and } n = K/A^2{}_0 = 2.85\times10^3.$$

Eq. (20) gives the relation between the amount of C. O. T. produced and the pressure of acetylene A. The calculated values from this equation of H at $i=4.6$ amp. are plotted against A in Fig. 7 and compared with the observed values. The agreement is satisfactory.

Acknowledgements are made to Mr. H. Shimojima of the Laboratory of Chemical Analysis of this Institute for his kind cooperation in carrying polarographic measurements, and to Dr. N. Hagiwara of the Osaka University who gave us a pure sample of C. O. T. We are indebted to the budget of the Ministry of Education for our experiments.

Laboratory of Physical Chemistry,
Tokyo Institute of Technology, Ōokayama, Tokyo

(14) *cf.* M. G. Evance and M. Szwarc, *Trans. Faraday Soc.*, **45**, 940 (1949).

The Structure of Surface-Denatured Protein. IV. The Molecular Weight, Surface Area and Shape of the Surface-Denatured Hemoglobin Molecule

By Kazutomo IMAHORI

(Received November 7, 1951)

In the previous three papers of this series the author has illustrated the apparatuses for measuring surface pressure and surface potential and by using these apparatuses, the molecular weight, surface area and shape of the surface denatured horse serum albumin have been measured.(1) And in the second paper a theory for the determination of the shape of the protein molecule has been developed.(2)

In this paper the structure of hemoglobin molecule is dealt with. As in the case of horse serum albumin, the molecular weight is first determined by H. B. Bull's method. Then the surface area is determined from the compressibility measurement. And finally the shape of the molecule is determined by the surface diffusion experiment.

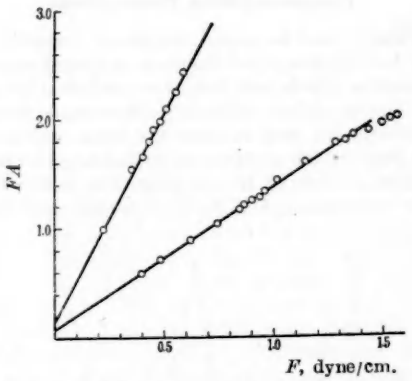


Fig. 1.—FA-F curves at pH = 6 and pH = 1.8.

Molecular Weight Determination

The method for the determination of molecular weight of surface denatured hemoglobin is just the same as that described in Part I.

Hemoglobin has been purified and crystallized from horse blood by Dr. T. Hosoya of the Institute of Science and Technology, Tokyo University, according to the ethanol method. About 0.2 M KCl solution was used as the substrate, because of the electric measurement purpose. Using the apparatus described in Part I and a thin glass plate, the result was obtained as shown in Fig. 1. The curve of Fig. 1 can be represented by the following equation being obtained by the least squares method:

$$FA = (0.064 \pm 0.017) + 1.32F \qquad (1)$$

Here, F means the surface pressure expressed in dyne/cm. and A means the surface area expressed in m.²/mg. From the equation (10) in Part I, the molecular weight of the surface-denatured hemoglobin is obtained as 35,000± 9,300, which is about a half of that of the native hemoglobin molecule, obtained by sedimentation, diffusion or osmotic pressure measurement.(3),(4) The result is reasonably accounted for by assuming that the hemoglobin molecule splits into two pieces by surface denaturation. This result agrees fairly well with that obtained recently by Michel and Benhamou.(5) Tonomura(6) has calculated the molecular weight of surface denatured hemoglobin to be about 4,000 from the data of Jonix(7) and has concluded that the hemoglobin molecule splits into about sisteen pieces when it is denatured on the surface. However, the measurement of Jonix was carried out under the surface pressure above 1 dyne/cm., and the result obtained by the extrapolation to zero pressure could hardly be expected to be correct. As shown in Fig. 1, the curve deviates from the straight line in the range above 1.5 dyn./cm. Now, if the curve above 1 dyne/cm. is extrapolated to zero pressure the FA value becomes far larger than that of the present experiment.

(1) K. Imahori, This Bulletin, **25**, 7 (1952) hereafter called Part I.
(2) K. Imahori, This Bulletin, **25**, 10 (1952) hereafter called Part II.
(3) N. Gralen, *Biochem J.*, **33**, 1907 (1939).
(4) Svedberg and Pedersen, "Die Ultrazentrifuge," p. 308 (1939).
(5) J. Michael and N. Benhamou, *Compt. rend.*, **228**, 1577 (1949).
(6) Y. Tonomura, *Kagaku*, **19**, 565 (1949).
(7) Jonix, *Biochem. Journ.*, **33**, 1745 (1939).

Guastalla[8] has measured the molecular weight of hemoglobin molecule expanded on the 0.01 *N* HCl solution and obtained the value of 12,000. The present author has measured the molecular weight of hemoglobin expanded on the ammonium sulphate solution of *p*H 1.8. The result is shown in Fig. 1 (curve b). The molecular weight is calculated to be 13,000± 2,800. These data may indicate that the molecule splits into four pieces.

Compressibility Measurment

The method for measuring the compressibility of hemoglobin is just the same as that of serum albumin which has been described in Part I. The modified Wilhelmy Balance is used. Hemoglobin used is from the same sample as is used in the previous experiment. Distilled water containing KCl is used as the substrate. As is shown in Fig. 2, the obtained curve has

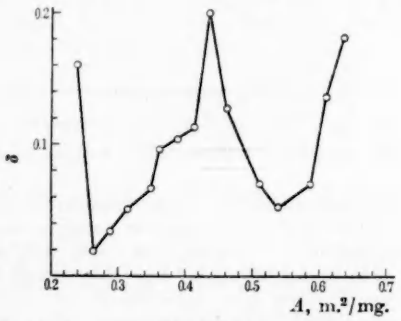


Fig. 2.—Compressibility of hemoglobin Film.

two minima. The one, A_m, is at the surface area of 0.535 m.²/mg. and the other, A_{2m}, is at the surface area of 0.262 m.²/mg. At the first minimum, compressibility, δ_m, is 0.054, and the surface pressure, F_m, is 17.1 dyn./cm., while at the second minimum δ_{2m} is 0.0197, and F_{2m} is 36.6 dyn./cm.

Taking into account that the molecular weight of the surface-dentatured horse hemoglobin is about 35,000 as obtained in the previous experiment, the area per one molecule is estimated te be 3065 Å.² at the first minimum. Davidson and others[9] have reported that horse methemoglobin is like a right-circular cylinder with the diameter of 57 Å. and the height of 34 Å.

The thickness of the hemoglobin film transferred on the metal surface under the surface pressure of about 16 dyn./cm. is measured by the optical method,[10] and found to be about 19 Å. This value is about one half of the height of the methemoglobin molecule described above. The molecular weight of the surface-denatured hemoglobin is about a half of that of the native one. Therefore, it is probable that the horse hemoglobin molecule splits into two pieces and takes the shape just as shown in Fig. 3.

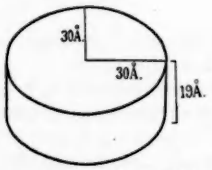


Fig. 3.—The shape of the surface-denatured hemoglobin molecule.

The area of the base of the cylinder-shaped methemoglobin molecule is calculated to be 2560 Å.² from the data by Davidson. On the other hand, even when this cylinder-shaped molecule is packed in one layer compactly on the water surface there is some space around each molecule and the area per one molecule should be about 10% larger than the area of the base of the cylinder, namely, 2816 Å.² per one molecule.

The area at the first minimum is obtained to be 3065 Å.² and this fact shows that the surface-denatured hemoglobin molecule at this point is in the state of closest packing.

If the film were compressed still more it would collapse, or two denatured homoglobin molecules would begin to join into the one original cylinder-shaped molecule. Taking into account that the A_{2m} is about one half of A_m, the film is considered to be doubled at the second minimum. Because, at A_{2m} one molecule covers about 1490 Å.² or two molecules cover about 2980 Å.², which is nearly equal to the above calculated value 2816 Å².

Moreover, δ_{2m} is somewhat smaller than one half of δ_m—the film at δ_{2m} is more than twice as incompressible as that at δ_m.

The Shape of the Surface-Denatured Horse Hemoglobin Molecule

From the result of the previous experiment it is supposed that the surface denatured hemoglobin molecule would have the shape as shown in Fig. 3.

The shape can be determined from the

(8) Guastalla, *Compt. rend.*, **208**, 1078 (1939).
(9) J. Bones-Watson, E. Davidson and M. F. Perutz, *Proc. Roy. Soc.*, **191A**, 83 (1947).
(10) K. Imahori and Y. Yoneyama, unpublished.

measurement of the diffusion constant on the surface. The theoretical treatment, on which the present experiment has its foundation, has been dealt with in Part II of this series.

The method for measuring the surface diffusion constant is just the same as that used in the case of serum albumin. Distilled water containing KCl is used as the substrate and castor oil is used as the balancing substances in the present case. The surface pressure is about 0.8 dyne/cm.

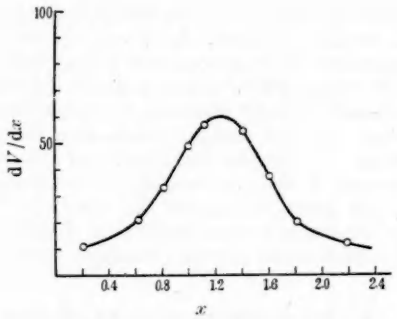


Fig. 4.—Concentration gradients after 7.2 hours of diffusion.

The result is shown in Fig. 4, which shows the gradients of surface potential at various points after 7.2 hours diffusion. In the figure, V means the surface potential expressed in Volt, and x means the distance expressed in cm. From this curve the diffusion constant is calculated, by the inflection point method, to be 2.78×10^{-6} cm.^{2}/sec. Using this value, and also other data such as $V=0.749$[4], $d=19$ Å. and $M=35{,}000$, f/f_0 is calculated from the equation (11) of part II to be 1.003. And thus c/a can be obtained from the Fig. 1 of Part II to be 1.12.

From this result it would seem that the surface-denatured hemoglobin molecule is an almost perfectly circular disk. In conclusion, the hemoglobin molecule is considered to split into two equal disks, the radius and the height of which are calculated to be about 30 Å. and about 19 Å., respectively, when it is denatured on the surface of the distilled water.

Summary

1. The molecular weight of the surface-denatured hemoglobin is calculated from the FA-F curve, to be about 35,000, which shows that the hemoglobin molecule splits into two pieces by surface denaturation at pH=6.

2. From the compressibility data, and surface denatured hemglobin molecule is considered to cover about 3065 Å.^{2} of area.

3. The ratio of two axes is obtained by the surface diffusion experiment to be 1.12.

4. The thickness of the molecule is determined to be 19 Å. by the optical method, and the surface-denatured hemoglobin molecule is considered to be a perfectly circular disk, the radius of which is about 30 Å. and the thickness about 19 Å.

The author wishes to express his hearty thanks to Prof. Henry B. Bull, Prof. Bun-ichi Tamamushi, Prof. San-ichiro Mizushima and Dr. Takehiko Shimanouchi for their kind discussions, advice and encouragement. This experiment is aided by the Scientific Research Grant of the Ministry of Education.

Chemical Institute, College of General Education, Tokyo University, Tokyo

On the Viscosity of Solutions of Non-electrolytes[1]

By Mikio TAMURA, Michio KURATA and Susumu SATA

(Received December 6, 1951)

1. Introduction

The viscosity of solutions composed of liquids (solvent) and solids (solute) can be treated from different standpoints: the first,[2] in which the solvents are regarded as the continuous medium and, then, the equations of Einstein's type based on the hydrodynamics are used; and the second, in which the solutions are regarded as the special case of the liquid mixture. Since the molecular sizes of solvent and of solute are comparable, inasmuch as the ordinary solutions, except polymer solutions, are concerned, it is obvious that the second viewpoint is more excellent than the first. The theory of Kendall and Monroe proposed in 1917 is probably the only treatment based on the second standpoint.[3] They extended their equation,

$$\eta^{1/3}=x_A\eta_A^{1/3}+x_B\eta_B^{1/3}, \qquad (1)$$

(which had been proposed for the viscosity η of the binary liquid mixture) to solutions of non-electrolytes such as benzene solution of naphthalene and calculated the "viscosity coefficient of solute" η_B as a parameter. According to them, η_B is a constant, independent of the concentration. But η_B of the same solute given by them shows different values from solvent to solvent as will be shown in Table 1. This is nothing but the illustration of the defect of Eq. (1), for η_B must be characteristic of the solute and independent of the nature of the solvents according to its definition.

Two of the present authors[4] proposed the following equation to represent the viscosity coefficient of a mixture of two liquids and showed that the equation agrees with the experimental data satisfactorily:

$$\eta=x_Aw_A\frac{d}{d_A}\eta_A+x_Bw_B\frac{d}{d_B}\eta_B+2\left(x_Ax_Bw_Aw_B\frac{d^2}{d_Ad_B}\right)^{1/2}\eta_{AB}, \qquad (2)$$

where x's denote the molar fractions, w's denote the weight fractions, d, d_A and d_B are the densities of the solution, the solvent and the solute respectively. η_{AB} is a parameter called "mutual viscosity coefficient", which has its origin in the mutual interaction between solvent and solute molecules, and is independent of the composition of the solution. In this paper, we applied the equation (2) to the benzene or toluene solutions of naphthalene or diphenyl and obtained reasonable results.

2. Independency of η_B in relation to the Nature of Solvent

We applied at first the equation (2) to the experimental data obtained by Kendall and Monroe.[3] In the case of a mixture of liquids, η_{AB} is the only unknown quantity that must be evaluated. In the present case, not only η_{AB} but also η_B is unknown. and we have two unknown parameters. To evaluate these, we rewrite Eq. (2) as follows:

$$\frac{\eta-(x_Aw_Ad/d_A)\eta_A}{x_Bw_Bd/d_B}=\eta_B+2\left(\frac{x_Aw_Ad/d_A}{x_Bw_Bd/d_B}\right)^{1/2}\eta_{AB}. \qquad (3)$$

If there occurs neither contraction nor expansion on mixing, then w_Ad/d_A etc. can be replaced by the volume fractions, φ_A etc., and we get

$$\frac{\eta-x_A\varphi_A\eta_A}{x_B\varphi_B}=\eta_B+2\left(\frac{x_A\varphi_A}{x_B\varphi_B}\right)^{1/2}\eta_{AB}. \qquad (4)$$

If we plot the value on the left hand side of the equation (4) against $(x_A\varphi_A/x_B\varphi_B)^{1/2}$, a straight line will be obtained so far as our equation is applicable. The results of our calculation give, indeed, straight lines as shown in Fig. 1; thus we can evaluate easily the values of η_B and η_{AB} in the usual way. As shown in Fig. 1, η_B, which is given by the ordinate of the point of intersection of the straight line and the ordinate, is constant, and is independent in relation to the nature of the

(1) Read at the 3rd annul meeting of the Society in April, 1950.
(2) For example, H. L. Bredeé and J. de Booys. *Kolloid Z.*, **91**, 39 (1940).
(3) J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, **39**, 1802 (1917).
(4) M. Tamura and M. Kurata, This Bulletin, **25**, 32 (1952).

solvent at a constant temperature. η_B is a kind of viscosity coefficient characteristic of the solute and should be independent of the solvent, as it is in our case, while η_B given by Kendall and Monroe depends upon the nature of the solvent, which is obviously inconsistent with the definition of η_B. The values of η_B and η_{AB} are given in Table 1.

Table 1

η_B and η_{AB} at 25°C. (Comparison of Eq. (2) with the Kendall and Monroe equation)

Solute / Solvent		Naphthalene		Diphenyl	
		Benzene	Toluene	Benzene	Toluene
K.-M. Eq.	η_B	2.25	1.825	3.44	2.82
Eq. (2)	η_B	1.98	1.92	2.87	2.85
	η_{AB}	1.030	0.912	1.197	1.004

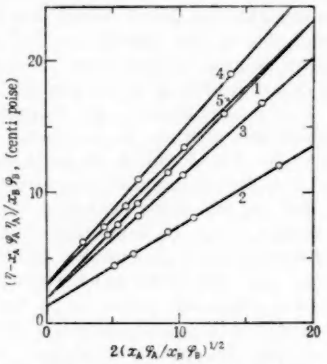


Fig. 1.—Comparison of Eq. (4) with experiments: lines 1, 2, benzene+naphthalene (25° and 60°C.); line 3, toluene+naphthalene (25°C.); line 4, benzene+Diphenyl (25°C.); line 5, toluene+diphenyl (25°C.).

3. Experimental

There are few data concerning the viscosity coefficient of such solutions as are under discussion, especially of solutions of high concentrations and those at various temperatures. So we conducted experiments on the viscosity of benzene solution of naphthalene. Benzene was purified in accordance with the instruction given by Richards and Schipley ("Organic Solvent" (1935)), and had melting point of 5.7°. Naphthalene was purified by sublimating twice in a vacuum and had a melting point of 80.0°.

In order to avoid the change in concentration due to the evaporation of benzene, we used the Ostwald type viscometer modified by Ostwald and Luther.[5] The temperature of the thermostat was regulated to ±0.005°. The measurements of the density and the viscosity were carried out at 25°, 30°, 40°, 50° and 60°. The results are shown in Table 2.

4. Temperature Dependency of η_B

In our calculation we used the equation (3). As for d_B at $t°$, the values calculated by the following equation were used,[6]

Table 2

Experimental Data of d, η and Calculated Values of η

A = Benzene and B = Naphthalene

100 x_B, %		0	2.82	6.90	8.98	13.41	15.87	20.89	25.33
100 w_B, %		0	4.55	10.85	13.93	20.27	23.63	30.23	35.76
25°C.	d	0.8733	0.8787	0.8883	0.8922	0.9009	0.9058	0.9169	0.9239
	η_{obs}	0.6020	0.6309	0.6732	0.6932	0.7423	0.7733	0.8330	0.8891
	η_{calc}		0.6298	0.6734	0.6957	0.7445	0.7730	0.8330	0.8871
	Δ		−0.2	0	+0.4	+0.3	0	0	−0.2
30°C.	d	0.8680	0.8736	0.8827	0.8872	0.8959	0.9007	0.9127	0.9170
	η_{obs}	0.5632	0.5882	0.6269	0.6448	0.6897	0.7181	0.7723	0.8222
	η_{calc}		0.5879	0.6268	0.6470	0.6912	0.7164	0.7723	0.8185
	Δ		−0.1	0	+0.3	+0.2	−0.2	0	−0.5
40°C.	d	0.8563	0.8634	0.8725	0.8771	0.8862	0.8908	0.9017	0.9097
	η_{obs}	0.4932	0.5160	0.5478	0.5665	0.6017	0.6263	0.6698	0.7200
	η_{calc}		0.5155	0.5487	0.5660	0.6041	0.6259	0.6749	0.7154
	Δ		−0.1	+0.2	−0.1	+0.4	−0.1	+0.7	−0.6
50°C.	d	0.8415	0.8529	0.8624	0.8666	0.8755	0.8807	0.8915	0.8992
	η_{obs}	0.4344	0.4564	0.4838	0.4993	0.5290	0.5509	0.5871	0.6319
	η_{calc}		0.4544	0.4824	0.4967	0.5296	0.5489	0.5909	0.6294
	Δ		−0.4	−0.3	−0.5	+0.1	−0.4	+0.6	−0.4
60°C.	d	0.8226	0.8425	0.8516	0.8551	0.8631	0.8705	0.8817	0.8894
	η_{obs}	0.3852	0.4059	0.4294	0.4418	0.4695	0.4925	0.5209	0.5572
	η_{calc}		0.4070	0.4308	0.4425	0.4695	0.4869	0.5211	0.5523
	Δ		+0.2	+0.3	+0.2	0	−1.2	0	−0.9

(5) See, for example, E. Hatschek, "The Viscosity of Liquids (London, 1928)," p. 47.

(6) International Critical Tables, Vol. III, (1928).

Table 3

Values of d_B, η_B and η_{AB} at Various Temperatures

Temp.	d_B	η_B	η_{AB}
25°C.	1.018	1.975	1.026
30	1.014	1.830	0.941
40	1.007	1.587	0.819
50	1.000	1.384	0.715
60	0.993	1.215	0.619

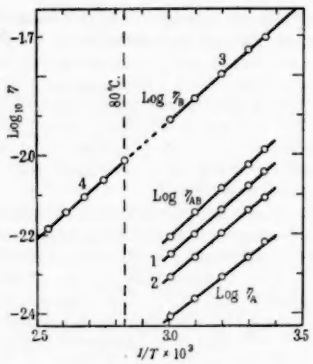


Fig. 2.—Temperature dependence of η of the system, benzene+naphthalene: line 1, $\log \eta$ ($x_B=0.2533$); line 2, $\log \eta$ ($x_B=0.1587$); line 3, $\log \eta_B$ (obtained by Eq. (3)); line 4, $\log \eta_B$ (liquid naphthalene)

$$d_B=0.9779+0.7670\times10^{-3}\times(80-t)-0.755\times10^{-6}\times(80-t)^2. \quad (5)$$

This equation holds for temperature higher than 80° (melting pt.). We extrapolated to lower temperatures to get d_B, for we thought it might be reasonable to use the densities of supercooled liquid naphthalene in our case. The values of d_B are shown in Table 3, with the values of η_B and η_{AB} at various temperatures which are obtained by the method mentioned in **2**. Using these values, we calculated the viscosity coefficient of the solutions. The results are given in Table 2 compared with the observed values. Δ in the table represents $100\times(\eta_{calc}-\eta_{obs})/\eta_{obs}$. The coincidence between the calculated and the observed values is very satisfactory.

Now let us investigate into the relation between η_B and the absolute temperature T. If η_B represents the "viscosity coefficient of naphthalene", it may satisfy the following equation, as is often the case with the viscosity coefficient of pure liquid in general.

$$\log \eta_B=a+(b/T), \quad (6)$$

where a and b are constants. In fact, the equation (6) is satisfied as shown in Fig. 2. (See the straight line No. 3 which lies to the right hand side of the dotted line indicating the melting point of naphthalene.) The straight line No. 4 in Fig. 2 is the plot of $\log \eta_B$ of the liquid naphthalene at temperatures higher than the melting point against $1/T$. Two plots, No 3 and No. 4, lie on a straight line, and this fact suggests an interesting conclusion that η_B, which we evaluated in **2** and in this section, may be none other than the viscosity coefficient of supercooled liquid naphthalene. And this shows that the coincidence between the observed values of η and the calculated values by eq. (2) is not a fictitious result coming from the regulation of the values of two parameters, η_B and η_{AB}.

In the lower part of the right hand side of Fig. 2, we plotted $\log \eta$ at various concentrations, $\log \eta_A$ and $\log \eta_{AB}$ against $1/T$, respectively. These give straight lines, whose slopes give the following activation energies of flow:

$\varepsilon_A=2.50$, $\varepsilon_B=2.74$ and $\varepsilon_{AB}=2.75$ kcal./mole.

Even in such a case as under discussion, where two components are rather similar to each other in construction, ε_{AB} is not always equal to $(\varepsilon_A+\varepsilon_B)/2$, and this fact indicates that the introduction of the term containing η_{AB} is necessary even in the case of apparently ideal solutions.

In conclusion, we wish to expess our thanks to Dr. S. Shida of Tokyo Institute of Technology for his kind and effective help concerning the experimental part, and also to acknowledge our indebtedness to the Ministry of Education for a grant-in-aid.

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University and Physico-chemical Laboratory, Tokyo Institute of Technology

(7) The experimental values of η_B of liquid naphthalene are as follows: 0.97(80°), 0.86(90°), 0.78(100°), 0.71(110°), 0.65(120°), 0.59(130°), 0.54(140°) and 0.49 centipoise (at 150°).
These values have been tabulated in K. Shiba, Tables of Physical Constants (in Japanese, Iwanami, Tokyo, 1947), p. 78.

Spectrochemical Study of Microscopic Crystals. II. Dichroism of Cobalt (III)-Praseo Salts

By Shoichiro YAMADA and Ryutaro TSUCHIDA

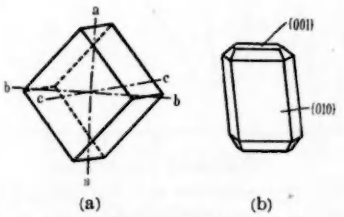
(Received December 7, 1951)

The crystal of the hydrochloride of the so-called "praseo-salts", 1, 6-dichloro-bis-(ethylenediamine)-Co(III) hydrochloride dihydrate, shows a striking dichroism, while that of the nitrate exhibits only a little dichroism compared with the former. This seems to be very interesting, being related to the fact that the hydrochloride easily effloresces in the air to lose its hydrogen chloride of crystallization and that the nitrate, stable in the air, is much less soluble than the hydrochloride. No research on these compounds, however, has been made in the crystalline state, nor has the analysis of the crystal structure or absorption spectrum of the crystal ever been reported. Previously, one of the present authors and M. Kobayashi, in the researches on pleochroism of the crystals of the metallic complex salts,[1] and the present authors, in the researches on dichroism of metallic planar complexes,[2],[3] showed that the measurement of pleochroism of the crystals was of great use to studies on the crystal structure and on the state of the complex ions in the crystals.

In this report, we can give the results of the measurement of dichroism with praseo-Co(III)-hydrochloride and nitrate, and discuss the orientations which the complex ions take in these crystals.

Experimental

Materials.—1, 6-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$[4] was prepared by the method of Werner.[5] The crystals obtained were green tablets on {001} bounded laterally by {110} (Fig. 1). These belong to the monoclinic system and exhibit extinction in the direction of the b- and the a-axis. The crystal shows marked dichroism in the above two directions, *i. e.*, blue by polarized light with electric vector parallel to the a-axis and yellow with a slight tint of green by that parallel to the b-axis. Analysis of the crystal structure has not been performed as yet. In this work dichroism measurement was made with microcrystals by light polarized in the above two directions.



(a) (b)

Fig. 1.—A modification of the crystal usually obtained: (a) praseo-hydrochloride dihydrate, (b) praseo-nitrate.

1, 6-$[Co(en)_2Cl_2]NO_3$ was prepared as green monoclinic crystals by adding concentrated nitric acid to the concentrated aqueous solution of the hydrochloride, acidified with hydrochloric acid. The crystals usually obtained are elongated in the c-direction, bounded by prism faces of {010} and {110} type. Very slight dichroism, as compared with the hydrochloride, can be observed in most faces, and the most distinct dichroism is found in {010}, *i. e.*, green by polarized light with electric vector parallel to the plane formed by the a- and the b-axis and greenish blue by that perpendicular to it. Dichroism measurement was made in that face by polarized light with electric vector in the above two directions. A little less distinct dichroism of a similar nature can be seen in {110}. Dichroism is discerned only slightly in {001} and {100}. The crystal structure has not been determined as yet.

Quantitative Dichroism Measurement.—The microscopic method[1],[6] was applied. The measurements were made with microcrystals of the respective salts by polarized light in the region covering about 7500 Å. to nearly 2000 Å. The crystals used in the measurements were several hundredths of mm. thick. The b- or a-absorption in Fig. 2 for the hydrochloride represents, respectively, absorption by polarized light with electric vector parallel to the b- or a-axis. $/\!/$- or $\perp$-absorption in Fig. 3 for the nitrate represents absorption by polarized light with electric vector parallel or perpendicular to the plane formed by the a-

(1) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka Japan (1944), (in Japanese).
(2) R. Tsuchida, S. Yamada and H. Yoneda, *J. Chem. Soc. Japan*, **69**, 145 (1948), (in Japanese).
(3) (a) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951); (b) This Bulletin, **24**, 125 (1951).
(4) en represents ethylenediamine molecule.
(5) A. Werner, *Ber.*, **34**, 1733 (1901).
(6) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951).

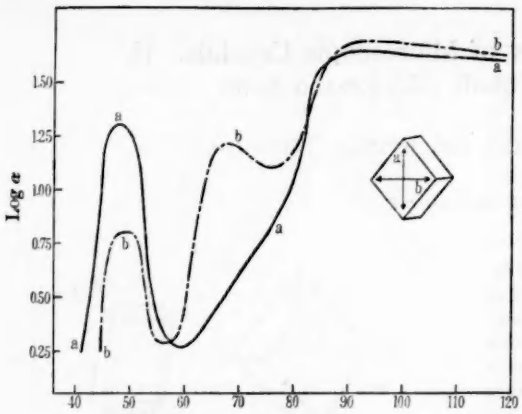


Fig. 2.—Dichroism of 1,6-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$.

and the b-axis. α denotes absorption coefficient per mm. of the crystal. Results of the measurements are shown in the figures 2 and 3, and summarized in Table 1.

Discussion

The Orientation of the Complex Ions in the Crystal of the Hydrochloride.—As is seen in Fig. 2, b- and a-absorption of the hydrochloride are quite different from each other. The difference between them is so large, as compared with that for planar complexes with four ligands, which was formerly determined,[6] that it may be inferred that all the complex ions take the same, at least almost the same, disposition in the crystal of this compound, since otherwise the crystal would not exhibit such a large difference between each of the absorptions. In the following, we shall discuss the orientations which the complex ions take in the crystal of the hydrochloride.

As to the first absorption band, a great difference in the extinction coefficient at the absorption maximum is observed between a- and b-abrorption, which we shall consider below. The transition probability in a certain direction for the first absorption band of a complex ion, which is considered as due to an electronic transition in an unsaturated transition shell,[7] can be, in general, supposed to be influenced most strongly by the ligands in that direction. On the basis of the above assumption the present authors found that there exists what we call "the hyperchromic series of ligands" which represents the decreasing order as to their effects on magnitude of molar extinction coefficient of a complex ion at an absorption maximum of its first absorption band.[8] In case of such a complex ion as 1, 6-$[Co(en)_2Cl_2]^+$, it is reasonable to suppose that the effect of ligands on transition probability for the first band in the direction connecting the central Co atom with two Cl atoms is quite different from that in the direction perpendicular to the above, *i.e.*, in the plane containing one Co and four N atoms of two ethylenediamine molecules around the central Co atom. Since ethylenediamine stands much higher in the hyperchromic series than Cl^-, it is supposed that the extinction coefficient of the first band is much larger for the absorption by polarized light with electlic vector in the en-Co-en plane than for that by polarized light with electric vector in the direction of the straight line, Cl-Co-Cl.

Thus, it is presumed that a-absorption in Fig. 2 corresponds to the absorption by polarized light with electric vector parallel to the en-Co-en plane, that the b-absorption corresponds to that by polarized light with electric vector in the Cl-Co-Cl direction, and, therefore, that in the crystal of the hydrochloride the line connecting Co at the center of a complex ion with two Cl atoms is parallel to the b-axis and that the plane containing Co and four N atoms of ethylenediamine molecules around Co is perpendicular to the b-axis of the crystal.

As to the second absorption band, a great difference in intensity as well as in the wave length at absorption maximum can be found between a- and b-absorption. In the same way as for the first band, the effect of ligands on the second absorption band is expected to be different in the en-Co-en plane from that in the direction of the straight line binding one Co and two Cl atoms. As for the order in hypsochromic effects of ligands on the second absorption band of metallic complexes, there have been known "the spectrochemical series,"[7] in which Cl stands much lower than ethylenediamine, meaning that Cl, as a ligand, has much more bathochromic effect on the second band of a complex than en. Therefore, it is suggested that the second absorption band by polarized light with electric vector in the direction of the line, Cl-Co-Cl, lies in the region of a considerably longer wave length than that

(7) R. Tsuchida, This Bulletin, 13, 388, 436 (1938).

(8) The report dealing with the subject will be submitted later.

perpendicular to the above, and, in consequence that the former corresponds to *b*-absorption and that the latter corresponds to *a*-absorption in Fig. 2.

From the foregoing discussion on the first and the second absorption band, it is inferred that all the complex ions take the same or at least almost the same disposition to the crystal axes in the crystal of the hydrochloride, that the straight line connecting Co and two Cl atoms is parallel to the *b*-axis, and that the plane containing Co and four N atoms of the two ethylenediamine molecules coincides with the plane formed by the *a*- and the *c*-axis.

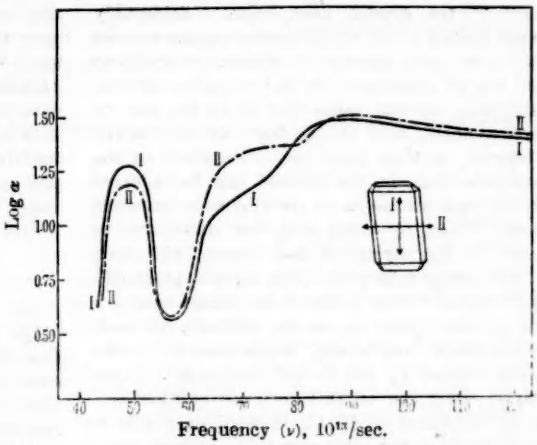


Fig. 3.—Dichroism of 1,6-$[Co(en)_2Cl_2]NO_3$.

Thus it is found that the dichroism of the praseo-hydrochloride in Fig. 2 represents that for the single ion, 1,6-$[Co(en)_2Cl_2]^+$ (Table 1). The dichroism of the single ion, as determined above, is in good accordance with the regularity as to the dichroism for the first and the second band of *trans*-disubstituted complex ions.[9] The fact that the nature of the dichroism for the first absorption band differs considerably from that for the second band suggests that the origins for those bands are different from each other. It was formerly stated[10] that extinction coefficients at absorption maxima of the first and the second band for complexes of some metals had almost equal magnitude, and it has been insisted that this is one of the principal grounds for the hypothesis that the first and the second band originate from similar transitions of electrons of the same kind. It is quite clear, however, that extinction coefficients at the absorption maxima of the first and the second band for the praseo-ion have remarkably different magnitudes in both the absorptions (Table 1) and that the two bands should be attributed to the electronic transitions of different kinds which are not related directly to each other.

Arrangement of the Complex Ions in the Crystal of the Praseo-nitrate and its Comparison with that of the Hydrochloride.—Since the dichroism for the crystal of the nitrate is found to be very slight as compared with that of the single praseo-complex ion, which has been determined from the dichroism measurement with the crystal of the hydrochloride, it must be presumed either that the complex ions in the crystal of the nitrate take considerably different orientations to one another, marked dichroism of single ions compensating for one another to such an extent that only a little dichroism is left in the crystal of the nitrate, or that the complex ions, all of which have the same orientations with refer-

Table 1

Absorption Maxima of Co(III)-Praseo-Ion

	1st Band		2nd Band		3rd Band	
Crystal	ν_{max}	$\log \alpha_{max}$	ν_{max}	$\log \alpha_{max}$	ν_{max}	$\log \alpha_{max}$
Cl-Co-Cl	48.7	0.80	68.0	1.21	flat	1.70
en-Co-en	48.0	1.30	(75)	—	flat	1.65
Solution[a]	ν_{max}	$\log \varepsilon_{max}$	ν_{max}	$\log \varepsilon_{max}$	ν_{max}	$\log \varepsilon_{max}$
	48.0	1.54	66.7	1.41	119.0	4.31
			78.9	1.64		

(a) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950). This measurement was made with Methanol-H_2O solution of praseo-chloride.

(9) Detailed report on the subject will be submitted later.

(10) K. Sone, *J. Chem. Soc. Japan*, **71**, 316 (1950). (in Japanese).

ence to the crystal axes, make considerably large angles to all of the three crystal axes so that absorption spectra in respective directions are not so distinctive as in the case of hydrochloride. In the same way as in the case of hydrochloride and on the basis of the results obtained in that case, the orientation of the complex ions in the nitrate can be inferred from observations as to the dichroism in some faces. Thus, by comparing the dichroism in {010} of the crystal of the nitrate with that of the single praseo-ion (Fig. 3), it is presumed that the en-Co-en plane of the praseo-complex ion in the crystal is, on the average, inclined at an angle considerably larger than 45° to the plane formed by the *a*- and the *b*-axis. Similarly, since the crystal does not exhibit distinct dichroism in {001}, showing only a little more greenish tone by polarized light with electric vector parallel to the *b*-axis than by polarized light perpendicular to it, it is supposed that the straight line, Cl-Co-Cl, in the complex ions makes to the *b*-axis an angle a little smaller than 45°, when viewed perpendicularly to the *ba*-plane. It is also suggested by comparing the nature of dichroism in {100} with that of the single complex ion that the straight line, Cl-Co-Cl, is, on the average, inclined to the *b*-axis at an angle only a little less than 45° when viewed perpendicularly to the *bc*-plane.

It seems that the complex ions are not usually arranged more disorderly in the crystal of the nitrate which contains planar nitrate ions than in the crystal of the hydrochloride with spherical chlorine ions instead of planar nitrate ions. Taking into consideration the fact that the crystal of the praseo-hydrochloride undergoes decomposition in the air at room temperature to give away one molecule of hydrogen chloride, it is suggested that the molecule of crystallization, HCl, plays an important part in holding the complex ions together so that all the complex ions take the same or at least almost the same orientation with their en-Co-en planes parallel to the *ac*-plane. This seems to be closely related to the fact that the violeo-salt in solution acidified with hydrochloric acid is readily changed into the praseo-salt and that the hydrochloride has not been found for the violeo-series whereas it is found for the praseo-series.

Summary

The dichroisms of 1,6-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and of 1,6-$[Co(en)_2Cl_2]NO_3$ have been measured by the microscopic method. From consideration of the results, it has been presumed that, in the crystal of the hydrochloride, the line connecting Co with two Cl atoms is almost parallel to the *b*-axis, that the plane containing one Co and four N atoms of two ethylenediamine molecules around Co is almost parallel to the plane formed by the *a*- and the *c*-axis. The nature of absorption bands of metallic complexes has been discussed on the basis of dichroism for the single praseo-ion, which has been determined from the above assumption. Arrangement of the complex ions in the nitrate has been inferred from observations as to the nature of dichroism in several faces. From comparison of the crystal structures of the two compounds and consideration of other properties, it has been suggested that the HCl molecule of crystallization in the crystal of the hydrochloride plays an important part in holding the complex ions together so that all the complex ions take the same orientation.

This investigation was supported in part by a grant from the Ministry of Education.

Department of Chemistry, Faculty of Science, Osaka University, Nakanoshima, Osaka

LETTER

Eine neue Bestimmungsmethode von Ligninsulfosäure in Sulfitzellstoffablauge

von Ryoichi SENJU

(Eingegangen am 11, Januar, 1952)

Um die Bestimmungsmethode von Ligninsulfosäure festzustellen, haben viele Forscher sich bisher vergebens angestrengt, von organischen Aminen ein gutes Fällungsmittel für Ligninsulfosäure zu entdecken. Ich wählte als Fällungsmittel ein neues hochmolekulares Amin (Polyglykolglucosamin), und es ist mir gelungen, die gesamte Ligninsulfosäure in Sulfitablauge damit quantitativ fällen zu lassen. Das Prinzip der Bestimmungsmethode besteht darin, dass man eine bekannte Menge von Polyglykolglucosamin (abgekürtzt P. G. G. A.) gegen das negative Polyvinylalkohol-Schwefelsäureester (abgekürtzt P. V. A. S.) zurückzutitriert.

Zu 5 cc. der zwanzigfach verdünnten Ablauge wird unter Umschütteln 5 cc. von $N/100$ P. G. G. A. (berechnet auf NH_2-Gruppe) zugesetzt. Ein Teil des Niederschlags der Ligninsulfosäure wird durch das überschüssige P. G. G. A. kolloid verteilt. Diese trübe Kolloidlösung wird gegen $N/400$ P. V. A. S. titriert. Sobald die äquivalente Menge von P. V. A. S zugesetzt ist, wird die trübe Lösung augenblicklich klar, und dann der Niederschlag sammelt sich flockig. Der Endpunkt dieser Kolloidtitration kann sehr genau bestimmt werden.

Bei der Titration der stark verdünnten Ablauge ist es vorteilhaft, Toluidinblau, das die stärke "Metachromasie" gibt, als Indikator zu benutzen. Wenn man das Gewicht des Niederschlags bei der Kolloidtitration wägen will, ist es zweckmässig, soviel Menge von Ablauge zu nehmen, wie man damit Niederschlags von 0.1-0.2 g. erhält.

Die Verbindung der negativen Ligninsulfosäure mit dem positiven P. G. G. A. weist ein sauberes stöchiometrisches Verhältnis auf. Daher ergibt sich aus dem Gewicht des ausgefällten Niederschlags die Menge der aus einem Mol NH_2-Gruppe entstehenden Verbindung.

Zieht man von diesem Gewicht das bekannte Äquivalentgewicht des verwendeten P. G. G. A. (C_8 H_{16} O_5 N=206) ab, so erhält man das Äquivalentgewicht der Ligninsulfosäure gegen NH_2-Gruppe (Tabelle 1, Spalte 5). Um die Ligninsulfosäure in Sulfitablauge zu bestimmen, braucht man aber nicht den Niederschlag bei der Kolloidtitration im einzelnen zu wägen, weil das Äquivalentgewicht von Ligninsulfosäure in Ablauge im allgemeinen Konstant(etwa 380) ist. Durch Verbrauch von P. G. G. A. kann man gleich die Menge der Ligninsulfosäure berechnen.

Diese Methode ist besonders darin überlegen, dass man die Bestimmung auf volumetrische Weise sehr genau und schnell ausführen kann. Deshalb ist diese Methode als eine Kontrollmethode für den Sulfitkochprozessverwendbar. Infolge des Mangels an schnellen Bestimmungs methoden von Ligninsulfosäure in Kochsäure sind die chemischen Techniker von Sulfitzellstoff-Fabriken dazu gezwungen, durch die mittelbaren Methoden wie die Bestimmung der Schwefligen Säure, des Farbtones und des spezifischen

Table 1

Die Bestimmung der Ligninsulfosäure in Kochsäure der Kunstseide Sulfit Zellstoff-Fabrik

1	2	3	4	5
Kochzeit in Min.	Verbrauch $N/100$ P. G. G. A. cc./cc. Ablauge	Niederschlag aus 1 cc. Lauge, g.	Ligninsulfosäure-Gehalt, g./cc.	Äquivalentgewicht von Ligninsulfosäure
420	19.13	0.1118	0.0724	378
450	21.40	0.1256	0.0815	381
480	24.27	0.1410	0.0910	375
510	24.66	0.1440	0.0932	379
570	25.00	0.1490	0.0975	394
600	26.38	0.1477	0.0954	376
690	26.05	0.1522	0.0985	378

Gewichtes von Kochsäure den Kochprozess zu kontrollieren. Daher glaube ich, dass diese Methode sowohl von den rein-wissenschaftlichen als auch von den technisch-wissenschaftlichen Forschern freudig angenommen wird.

Institut für Wissenschaft und Industrie der Universität Kyushu

On the Constituent Amino Acids, *N*-Terminal Residues and the Molecular Weights of Protamines[1]

By Toshio ANDO, Shin-ichi ISHII, Chieko HASHIMOTO, Makoto YAMASAKI and Koichi IWAI

(Received March 8, 1952)

Each sample of crude protamines, clupein and salmine, was tentatively fractionated into two parts, namely the more and the less soluble parts, making use of the different solubilities of their picrates in 67% aqueous acetone, and they were then purified to yield colorless crystal-like sulfates respectively[2].

The following amino acids were found as the constituents in the purified specimens of protamines by means of paper chromatography of their hydrolysates respectively: Arg, Pro, Ala, Val, Ser, Thr, Iso (or Leu) and Gly in both the more and the less soluble clupein; Arg, Pro, Ser, Val, Gly, Ala and Iso (or Leu) in the less soluble salmine. Thus, while no other amino acid than those heretofore known[3,4,5] was found in salmine, glycine was now found for the first time, besides the other constituents[4,6,7], in each specimen of our clupein. The probability of an occurrence of glycine from the contaminated nucleic acid can be excluded, as the ultraviolet absorption of the specimens in solution showed no presence of the above acid. Between the less and the more soluble clupein, some differences could be found in the relative contents of the constituent amino acids. Studies are now in progress with respect to the nature as well as the homogeneity of the soluble substances.

Further results were obtained, showing that salmine (the less soluble) has indeed proline[8,5] as the only *N*-terminal residue of the peptide molecule, being proved by means of the DNP-method[9] followed by paper chromatographic and spectrophotometric methods, and has a molecular weight of *ca.* 7,300 as the free base estimated tentatively[10] from the methoxyl content (0.34%) of the methyl ester sulfate, which was prepared under a mild condition of esterification.[11] In the case of the less soluble specimen of our clupein, it has, contrary to the recent results of German researchers,[6] alanine but not proline as the *N*-terminal residue, being confirmed on paper chromatograms not only as the DNP-alanine[12] produced but also as the free alanine regenerated[13] therefrom, and it is assumed[10] to have a molecular weight of *ca.* 10,800 as the free base from the methoxyl content (0.23%) of the ester sulfate. Contrary to the old view that salmine is about twice as large as clupein, both protamines seemed thus to have the molecular weight of nearly the same order.

The electrometric titration of the protamines and the ultraviolet absorption of the DNP-clupein (λ_{max}: 358-360 and 257-260 mμ at pH=9.1) and of the DNP-salmine (λ_{max}: 372-375 mμ at pH=9.1) seemed to give further results consistent with those obtained above for their *N*-terminal residues. Details of these experiments will be reported later.

Institute of Science and Technology, Tokyo University, Komaba-machi, Meguro-ku, Tokyo

(1) The present paper was read by one of the authors (T. A.) before the symposiums on protein structure held on May 20, 1951 in Osaka University and on Febr. 16, 1952 in Tokyo University.

(2) T. Ando, *et al.*, *Repts. Radiation Chem. Res. Inst. Tokyo Univ.*, **3**, 14 (1948); **4**, 31 (1949); **5**, 36 (1950).

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(10) The assumption is made that the purification of the ester is accomplished.

(11) H. Fraenkel-Conrat, *et al.*, *J. Biol. Chem.*, **161**, 259 (1945).

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Atomic Polarization of Aliphatic Alcohols in the Liquid state

By Masasi YASUMI, Michio SHIRAI and San-ichiro MIZUSHIMA

(Received March 15, 1952)

The refractive index n and absorption coefficient k of methyl, ethyl, *i*-propyl, *n*-butyl,

Table 1.

	methyl alcohol	ethyl alcohol	*i*-propyl alcohol	*n*-butyl alcohol	*i*-butyl alcohol	*tert*-butyl alcohol
ε_0	31.5	24.3	18.0	16.0	16.0	9.90
ε' (3.24 cm.)	5.55	4.08	3.06	3.08	2.94	2.80
ε''(3.24 cm.)	5.12	2.58	1.18	1.08	1.01	0.85
n_D^2	1.76	1.85	1.89	1.95	1.94	1.92

Table 2.

	methyl alcohol	ethyl alcohol	*i*-propyl alcohol	*n*-butyl alcohol	*i*-butyl alcohol	*tert*-butyl alcohol
ε_∞	4.54	3.76	2.96	2.99	2.86	2.70
P_E	8.2	13.0	17.6	22.1	22.2	22.2
M/d	40.7	58.6	79.6	91.9	92.9	94.8
$\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\frac{M}{d}$	22.1	28.7	30.4	36.6	35.5	34.3
P_A	13.9	15.7	12.8	14.5	13.3	12.1

i-butyl, and *tert*-buthyl alcohols have been measured at the wave length of 3.24 cm. and at the temperature of 25°C. by the improved free wave method reported previously.[1] From the values of n and k the dielectric constant ε' and the loss factor ε'' have been calculated through the following equation.

$$\varepsilon'-i\varepsilon''=(n-ik)^2 \qquad (1)$$

The calculated values are shown in Table 1 with the static dielectric constant ε_0 and the square of refractive index n_D^2 for D-line.

If we assume a single relaxation time, we have the following relations irrespective of the dielectric model

$$\varepsilon'=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2}=\varepsilon_\infty+\frac{\varepsilon_0-\varepsilon_\infty}{1+(\lambda_s/\lambda)^2} \qquad (2)$$

$$\varepsilon''=\frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2}\omega\tau=\frac{\varepsilon_0-\varepsilon_\infty}{1+(\lambda_s/\lambda)^2}(\lambda_s/\lambda) \qquad (2)$$

$$\lambda_s=2\pi c\tau \qquad (4)$$

where τ is the relaxation time corresponding to a critical wave length λ_s (Sprungswellenlänge) and λ, ω, and c have their usual significance. ε_∞ is the value of ε' at high frequencies at which the orientation effect of dipole disappears completely. The values of ε_∞ shown in Table 2 (and those of λ_s) have been chosen as to give the best fit with the experimental data through Fqs. (2), (3) and (4). From ε_∞ we can calculate the values of atomic polarization P_A by the following equation:

$$P_A=\frac{\varepsilon^\infty-1}{\varepsilon_\infty+2}\frac{M}{d}-P_E$$

where M is the molecular weight, d the density, $P_E=\frac{n_D^2-1}{n_D^2+2}\frac{M}{d}$ the electronic polarization for D-line. The vaules of $\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\frac{M}{d}$, P_E and P_A are shown in Table 2.

We see that the atomic polarization of each alcohol in the liquid state has almost the same value which is about 14 cc. and is much larger than that in the gaseous state which is estimated as less than 10% of the electronic polarization: *i.e.* less than 2 cc.

The large values of atomic polaization of these alcohols in the liquid state are, therefore, attributable to the structure of the liquid and the approximate constancy of these values may be explained by considering that the hydrogen bond plays the most important part in this problem.

Detailed discussion will be published elsewhere.

Institute of Science and Technology
and Faculty of Science of Tokyo University

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